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<b>(21) International Application Number:</b> PCT/US96/12380 <b>(22) International Filing Date:</b> 29 July 1996 (29.07.96)  <b>(30) Priority Data:</b> 60/001,687 31 July 1995 (31.07.95) US Not furnished 18 July 1996 (18.07.96) US  <b>(71) Applicant:</b> FMC CORPORATION [US/US]; 1735 Market Street, Philadelphia, PA 19103 (US). <b>(72) Inventor:</b> QUIRK, Roderic, P.; 66 Southwood Road, Akron, OH 44313 (US). <b>(74) Agent:</b> KENNEDY, Robert, M.; FMC Corporation, 1735 Market Street, Philadelphia, PA 19103 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> STAR POLYMERS FROM MIXED INITIATORS		
<b>(57) Abstract</b>  The present invention provides novel, multi-arm or star-shaped polymers having mixed protected functional and non-functional ends, their optionally hydrogenated analogues, and the polymers produced by removal of the protecting groups. The invention also provides a process for the preparation of novel multi-arm or star-shaped polymers having branched-end functionality on some, but not all, of the branches. The multi-arm or star polymers of this invention are produced from more than one type of initiator, i.e., from both functional and non-functional initiators which, by design, incorporates both desired physical properties associated with multi-arm or star polymers with non-functional branch-ends and the versatility of functional branch end multi-arm or star polymers.  		

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## STAR POLYMERS FROM MIXED INITIATORS

5           This invention concerns novel, multi-branched or star-shaped polymers having mixed protected functional and non-functional ends, their optionally hydrogenated analogues, the polymers produced by removal of the protecting groups, and the processes to prepare these polymers.

## 10                           BACKGROUND OF THE INVENTION

Multi-branched or star-shaped polymers were described by Zelinski in U. S. Patent 3,280,084, in which polybutadiene anion (generated by addition of butyllithium to butadiene) was coupled with 0.02 to 1 part by weight of  
15   divinylbenzene to 100 parts of monomer. The resultant star polymer had a polydivinylbenzene core and several identical arms of polybutadiene radiating from the core. The arms could also be either random or block copolymers of styrene and butadiene, wherein the diene is the major component. The synthesis of star polymers with arms of different molecular  
20   weights was disclosed by Kitchen et al, U. S. Patent 3,639,517. Fetters and Bi, U. S. Patent 3,985,830, detailed the preparation of star polymers with a nucleus of more than one molecule of divinylbenzene, and more than three arms. These polymers were formed by addition of living homopolymers and copolymers of conjugated diene monomers and block copolymers of  
25   conjugated diene monomers and monovinylaromatic monomers to divinylbenzene. These unfunctionalized star polymers have been employed as viscosity index (V.I.) improvers for lube oil compositions (see for example, U. S. Patents Nos. 5,310,490 and 5,310,814).

Star polymers have also been prepared which contain functionality,  
30   such as hydroxy groups, at the ends of the arms. For instance, European Patent Application 0632075, disclosed the preparation of star molecules with

- 2 -

hydroxyl groups generated at the terminus of each living arm of the star. However, these functionalization reactions are often inefficient, due to the formation of physical gelation phenomena that produce severe mixing problems (see L. Weber, Makromol. Chem., Macromol. Symp., 3, 317 (1986) and U. S. Patent Nos. 5,393,843 and 5,478,899). These polymers were prepared by addition of ethylene oxide to the living anions at the ends of the arms of the star polymer. These functionalized star polymers were useful in making adhesives, sealants, coatings, films and fibers.

10

## SUMMARY OF THE INVENTION

The current invention concerns novel, multi-branched or star-shaped polymers having both protected functional and non-functional ends, their optionally hydrogenated analogues, the polymers produced by removal of the protecting groups, and the processes to prepare these polymers.

15

## DESCRIPTION OF THE INVENTION

The present invention concerns novel, multi-branched or star-shaped polymers having mixed protected functional and non-functional ends, their optionally hydrogenated analogues, and the polymers produced by removal of the protecting groups. The invention also describes a process for the preparation of novel multi-branched ("star"-shaped) polymers having branched-end functionality on some, but not all, of the branches. The star polymers of this invention are unique in that they are produced from more than one type of initiator, i.e., from both functional and non-functional initiators which, by design, incorporates both desired physical properties associated with non-functional branch end star polymers and the versatility of functional branch end star polymers. For example, non-functional branches in the polymer provide improved impact resistance in the final polyester or polyamide molecules derived by copolymerization of hydroxy-,

20  
25  
30

thio-, or amino- terminated functional branches in the polymer with comonomers such as dicarboxylic acids and diisocyanates.

Novel multi-arm or star-shaped polymers having both functional and non-functional ends are produced by polymerizing conjugated alkadienes, comprising the group of butadiene and isoprene, or alkenylsubstituted aromatic compounds, comprising the group of styrene and alpha-methylstyrene, either singly, sequentially, or as mixtures thereof, with mixtures of (a) alkyllithium initiators, comprising the group of n-butyllithium, sec-butyllithium, and tert-butyllithium and (b) protected functional organolithium initiators, having the formula:



where Q is an unsaturated hydrocarbyl group derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds, or mixtures of one or more dienes with one or more alkenylaromatic compounds into the Li-Z linkage at a carbon-lithium bond thereof ; Z is defined as a branched or straight chain hydrocarbyl connecting group containing 3 to 25 carbon atoms; T is an element selected from the group of oxygen, sulfur, and nitrogen; (A-R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>)<sub>m</sub> is a protecting group in which A is an element selected from Group IVa of the Periodic Table of the Elements as exemplified by carbon and silicon; R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms; m is 1 when T is oxygen or sulfur and 2 when T is nitrogen; and n is an integer from 0 to 5; to produce protected "living" polymer anions which are subsequently reacted with polyfunctional linking compounds, comprising the group of silicon tetrachloride, methyltrichlorosilane, tin tetrachloride (as described in U. S. Patent No.

3,639,517 and by R.P.Zelinski et al in J.Polym.Sci., A3, 93, (1965)), phosphorus trichloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes, or mixtures thereof. Removal of the protecting group (deprotection) produces multi-arm or star polymers with hydroxyl, sulfhydryl, or amino groups on the ends of the polymer arms that had been terminated with protecting groups. The residual aliphatic unsaturation can be optionally removed by hydrogenation before or after removal of the protecting groups. These functional groups can then participate in various copolymerization reactions by reaction of the functional groups on the ends of the arms of the polymer with a selected difunctional or polyfunctional comonomer or comonomers selected from the group consisting of organic dicarboxylic acids, organic polycarboxylic acids, organic diisocyanates, organic polyisocyanates, organic diamides, organic polyamides, cyclic amides, organic diols, organic polyols, ethylene oxide in the presence of potassium butoxide, and methacryloyl chloride, acryloyl chloride, or styrenyldimethylchlorosilane, the last three of which are subsequently reacted with a free radically polymerizable monomer.

This linking process is described in U. S. Patent No. 4,409,357 and by L.J.Fetters in Macromolecules, 9, 732, (1976). These radiating multi-arm or star polymers with protected functionality on the ends of some, but not all, of the arms may be optionally hydrogenated before or after removal of the protecting groups. The multi-arm or star polymers thus formed may have hydroxyl, sulfhydryl (thio), or amino functional branch ends as well as non-functional branch ends which serve to modify the physical properties of these star-shaped or multi-arm radiating polymers, especially after their further copolymerization with other functional monomers, such as organic diacids or organic diisocyanates.

The protected functional initiators of formula (I) comprise the group of omega-(tert-alkoxy)-1-alkyllithiums, omega-(tert-alkoxy)-1-alkyllithiums chain extended with conjugated alkadienes, as exemplified by isoprene, or alkenylsubstituted aromatics, as exemplified by styrene, omega-(tert-

alkylthio)-1-alkyllithiums, omega-(tert-alkylthio)-1-alkyllithiums chain extended with conjugated alkadienes, as exemplified by isoprene, or alkenylsubstituted aromatics, as exemplified by styrene, omega-(tert-butyltrimethylsilyloxy)-1-alkyllithiums, omega-(tert-butyltrimethylsilylthio)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums chain-extended with conjugated alkadienes, as exemplified by isoprene, or alkenylsubstituted aromatics, as exemplified by styrene, and omega-(bis-tert-alkylsilylamino)alkyllithiums.

In another aspect of this invention, novel multi-branched or star-shaped polymers possessing both functional and non-functional ends may also be produced by separately polymerizing, either singly, sequentially, or as mixtures thereof, conjugated alkadienes, as exemplified by butadiene and isoprene, and alkenylsubstituted aromatic compounds, as exemplified by styrene and alpha-methylstyrene, with (a) alkyllithium initiators, comprising the group of n-butyllithium, sec-butyllithium, and tert-butyllithium, and with (b) protected functional organolithium initiators, having the formula:



where Q is an unsaturated hydrocarbyl group derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds, or mixtures of one or more dienes with one or more alkenylaromatic compounds into the Li-Z linkage at a carbon-lithium bond thereof; Z is defined as a branched or straight chain hydrocarbyl connecting group containing 3 to 25 carbon atoms; T is an element selected from the group of oxygen, sulfur, and nitrogen;  $(\text{A-R}^1\text{R}^2\text{R}^3)_m$  is a protecting group in which A is an element selected from Group IVa of the Periodic Table of the Elements as exemplified by carbon and silicon;  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, lower

dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms; m is 1 when T is oxygen or sulfur and 2 when T is nitrogen; and n is an integer from 0 to 5; subsequently mixing the resulting separately produced "living" polymer anions, treating the resulting  
5 mixture with polyfunctional linking compounds, comprising the group of silicon tetrachloride, methyltrichlorosilane, tin tetrachloride, phosphorus trichloride, isomeric diisopropenylbenzenes and the isomeric divinylbenzenes (see references cited above), and optionally hydrogenating before or after optionally deprotecting the functional ends of the polymer.

10 This alternative method allows for independent control of the molecular weight of the arms of the multi-arm or star polymer and provides for a more selective control of the physical properties of the resultant polymers. Removal of the protecting group (deprotection) produces multi-arm polymers with hydroxyl, sulfhydryl (thio), and amino or substituted amino functional  
15 groups on the ends of the polymer arms that had been terminated with protecting groups. The residual aliphatic unsaturation can be optionally removed by hydrogenation before or after removal of the protecting groups. These functional groups can then participate in various copolymerization reactions by reaction of the functional groups on the ends of the arms of the  
20 polymer with a selected difunctional or polyfunctional comonomer or comonomers selected from the group comprising organic dicarboxylic acids, organic polycarboxylic acids, organic diisocyanates, organic polyisocyanates, organic diamides, organic polyamides, cyclic amides, organic diols, organic polyols, ethylene oxide in the presence of potassium  
25 butoxide, and methacryloyl chloride, acryloyl or styrenyldimethylchlorosilane the last three of which can be subsequently reacted with a free radically polymerizable monomer.

The protected functional initiators of formula (I) comprise the group of omega-(tert-alkoxy)-1-alkyllithiums, omega-(tert-alkoxy)-1-alkyllithiums chain  
30 extended with conjugated alkadienes, as exemplified by isoprene, or alkenylsubstituted aromatics, as exemplified by styrene, omega-(tert-

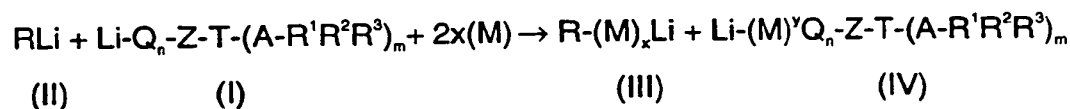


alkylthio)-1-alkyllithiums, omega-(tert-alkylthio)-1-alkyllithiums chain extended with conjugated alkadienes, as exemplified by isoprene, or alkenylsubstituted aromatics, as exemplified by styrene, omega-(tert-butyltrimethylsilyloxy)-1-alkyllithiums, omega-(tert-butyltrimethylsilylthio)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums chain-extended with conjugated alkadienes, as exemplified by isoprene, or alkenylsubstituted aromatics, as exemplified by styrene, and omega-(bis-tert-alkylsilylamino)alkyllithiums.

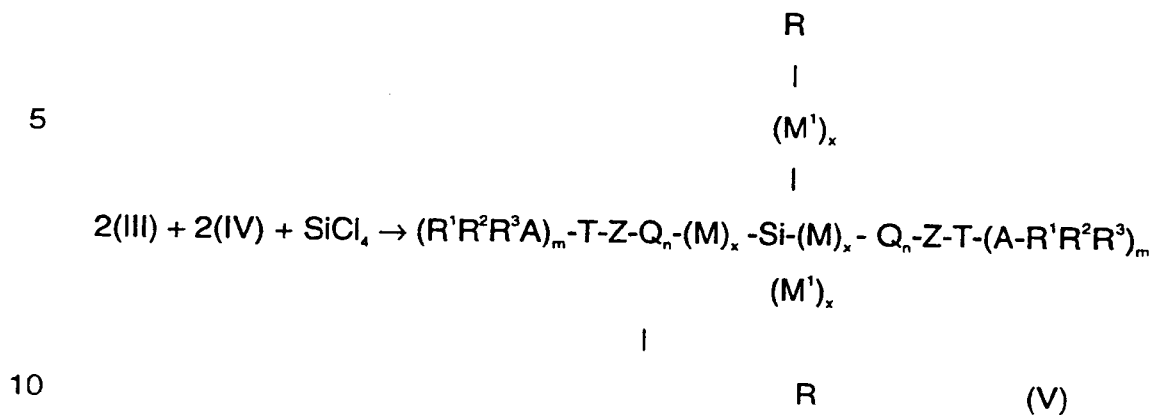
In contrast to star polymers of the prior art, the molecular architecture of compounds of the present invention can be more precisely controlled. The ratio of protected functionalized arms to non-functionalized arms can be adjusted by simply varying the ratio of protected functional initiator to alkyllithium initiator, or the ratio of the polymers prepared separately from these initiators. The mole percent of protected functional initiator in the total charge of initiator is between 2 and 98. Further, the monomer identity, the monomer composition and molecular weight of both the functional and non-functional arms can be independently manipulated by varying the monomer charged to each initiator. Finally, the number of polymer arms can be adjusted by varying the nature of the coupling agent, and by varying the ratio of living polymer to the coupling agent.

Idealized reaction equations shown below using equivalent amounts of functional and non-functional initiators, a single monomer, a common polymerization reactor, and the linking agent silicon tetrachloride serve to further clarify the process:

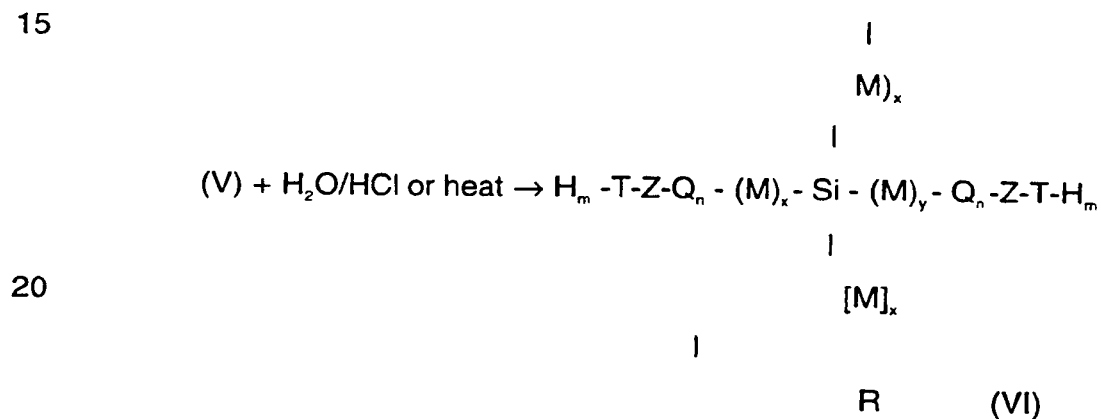
## Equation 1



## Equation 2



## Equation 3



Formula (II) above represents a simple organolithium initiator where  
 R is alkyl. Formula (I) above represents a protected functional organolithium  
 initiator, where Q is an unsaturated hydrocarbyl group derived by  
 incorporation of one or more conjugated diene hydrocarbons, one or more  
 alkenylaromatic compounds, or mixtures of one or more dienes with one or  
 more alkenylaromatic compounds into the M-Z linkage at a carbon-lithium  
 bond ; Z is defined as a branched or straight chain hydrocarbyl connecting  
 group containing 3 to 25 carbon atoms; T is an element selected from the

group of oxygen, sulfur, and nitrogen;  $(A-R^1R^2R^3)_m$  is a protecting group in which A is an element selected from Group IVa of the Periodic Table of the Elements as exemplified by carbon and silicon;  $R^1, R^2$ , and  $R^3$  are independently selected from hydrogen, alkyl, substituted alkyl groups  
5 containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms; m is 1 when T is oxygen or sulfur and 2 when T is nitrogen; n is an integer from 0 to 5, and x and y are  
10 independently integers defining the number of monomer units M.

Examples of organolithium initiator (II) include, but are not limited to, ethyllithium, isopropyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium, n-hexyllithium, n-octyllithium, and 2-ethylhexyllithium or mixtures thereof.

Examples of protected functionalized organolithium initiators (I)  
15 include, but are not limited to, tert-alkoxy-alkyllithiums such as 3-(1,1-dimethylethoxy)-1-propyllithium and its more hydrocarbon-soluble isoprene chain-extended oligomeric analog (n=2 in formula (I) above), 3-(tert-butyldimethylsilyloxy)-1-propyllithium (n=0), tert-alkylthio-alkyllithiums such as 3-(1,1-dimethylethylthio)-1-propyllithium and its more hydrocarbon-  
20 soluble isoprene chain-extended oligomeric analog (n=2), 3-(dimethylamino)-1-propyllithium and its more hydrocarbon-soluble isoprene chain-extended oligomeric analog (n=2) and 3-(di-tert-butyldimethylsilylamino)-1-propyllithium, and mixtures thereof. Further examples of protected functionalized initiators that may be employed in this  
25 invention include, but are not limited to: 3-(1,1-dimethylethoxy)-1-propyllithium, 3-(1,1-dimethylethoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethoxy)-1-butyllithium, 5-(1,1-dimethylethoxy)-1-pentyllithium, 6-(1,1-dimethylethoxy)-1-hexyllithium, 8-(1,1-dimethylethoxy)-1-octyllithium, 3-(1,1-  
30 dimethylpropoxy)-1-propyllithium, 3-(1,1-dimethylpropoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-

dimethylpropoxy)-1-butyllithium, 5-(1,1-dimethylpropoxy)-1-pentyllithium, 6-(1,1-dimethylpropoxy)-1-hexyllithium, 8-(1,1-dimethylpropoxy)-1-octyllithium, 3-(t-butyldimethylsilyloxy)-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 4-(t-butyldimethylsilyloxy)-1-butyllithium, 5-(t-butyldimethylsilyloxy)-1-pentyllithium, 6-(t-butyldimethylsilyloxy)-1-hexyllithium, 8-(t-butyldimethylsilyloxy)-1-octyllithium and 3-(trimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 3-(dimethylamino)-1-propyllithium, 3-(dimethylamino)-2-methyl-1-propyllithium, 3-(dimethylamino)-2,2-dimethyl-1-propyllithium, 4-(dimethylamino)-1-butyllithium, 5-(dimethylamino)-1-pentyllithium, 6-(dimethylamino)-1-hexyllithium, 8-(dimethylamino)-1-propyllithium, 3-(hexamethyleneimino)-1-propyllithium, 4-(hexamethyleneimino)-1-butyllithium, 5-(hexamethyleneimino)-1-pentyllithium, 6-(hexamethyleneimino)-1-hexyllithium, 8-(hexamethyleneimino)-1-octyllithium, 3-(t-butyldimethylsilylthio)-1-propyllithium, 3-(t-butyldimethylsilylthio)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilylthio)-2,2-dimethyl-1-propyllithium, 4-(t-butyldimethylsilylthio)-1-butyllithium, 6-(t-butyldimethylsilylthio)-1-hexyllithium, 3-(trimethylsilylthio)-2,2-dimethyl-1-propyllithium, 3-(1,1-dimethylethylthio)-1-propyllithium, 3-(1,1-dimethylethylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylethylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethylthio)-1-butyllithium, 5-(1,1-dimethylethylthio)-1-pentyllithium, 6-(1,1-dimethylethylthio)-1-hexyllithium, 8-(1,1-dimethylethylthio)-1-octyllithium, 3-(1,1-dimethylpropylthio)-1-propyllithium, 3-(1,1-dimethylpropylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropylthio)-1-butyllithium, 5-(1,1-dimethylpropylthio)-1-pentyllithium, 6-(1,1-dimethylpropylthio)-1-hexyllithium, and 8-(1,1-dimethylpropylthio)-1-octyllithium. and their more hydrocarbon soluble conjugated alkadiene or alkenylsubstituted aromatic chain extended oligomeric analogs (n = 1-5 in formula (I) above).

Protected functional organolithium initiators of the formula  $\text{Li-Z-T-(A-R}^1\text{R}^2\text{R}^3)_m$  (VII) which general formula represents the compound types  $\text{Li-Z-O-CR}^1\text{R}^2\text{R}^3$ ,  $\text{Li-Z-O-SiR}^1\text{R}^2\text{R}^3$ ,  $\text{Li-Z-N-(CR}^1\text{R}^2\text{R}^3)_2$ ,  $\text{Li-Z-N-(SiR}^1\text{R}^2\text{R}^3)_2$ ,  $\text{Li-Z-S-CR}^1\text{R}^2\text{R}^3$ , and  $\text{Li-Z-S-SiR}^1\text{R}^2\text{R}^3$ . are prepared by reacting their respective

5 organic halides,  $\text{Cl-Z-T-(A-R}^1\text{R}^2\text{R}^3)_m$ , (general formula representing all six of the above shown formulas), with lithium metal in an inert, hydrocarbon solvent medium at reaction temperatures up to the reflux temperature of the solvent.

Incorporation of Q groups into the Li-Z linkage to form the compounds

10 of formula (I) above involves addition of compounds of the formula  $\text{Li-Z-T-(A-R}^1\text{R}^2\text{R}^3)_m$  (VII) where the symbols have the meanings ascribed above, across the carbon to carbon double bonds in compounds selected from the group of conjugated dienes and alkenylsubstituted aromatic hydrocarbons to produce new carbon-lithium bonds of an allylic or benzylic nature. These

15 new carbon-lithium bonds are much like those found in a propagating polyalkadiene or polyarylethylene polymer chains derived by anionic initiation of the polymerization of conjugated dienes or arylethylenes. These new carbon-lithium bonds are now "activated" toward polymerization and so are much more efficient in promoting polymerization than the precursor Li-Z

20 bonds, themselves.

Thus, the initiators of the formula  $\text{Li-Q}_n\text{-Z-T-(A-R}^1\text{R}^2\text{R}^3)_m$  (I) are prepared by reacting a compound of the formula  $\text{Li-Z-T-(A-R}^1\text{R}^2\text{R}^3)_m$  (VII), wherein Z, T, A,  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and m have the meanings ascribed above, with one or more conjugated diene hydrocarbons, one or more alkenylaromatic

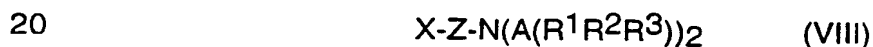
25 compounds, or mixtures of one or more dienes with one or more alkenylsubstituted aromatic compounds, to form an extended hydrocarbon chain between Li and Z in formula which extended chain is denoted as  $\text{Q}_n$  in formula (I) where n is an integer between 1 and 5. The compounds of formula (VII) are prepared by first, reacting in an inert solvent, a selected

30 tertiary amino-1-haloalkane or an omega-hydroxy-protected-1-haloalkane or an omega-thio-protected-1-haloalkane, depending on whether "T" is to be N,

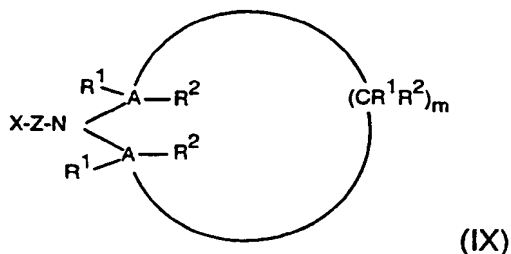
O or S, (the alkyl portions of the haloalkyl groups contain 3 to 25 carbon atoms) with an alkali metal, preferably lithium, at a temperature between about 35 °C and about 130 °C, preferably at the solvent reflux temperature, to form a protected monofunctional lithium initiator (of formula VII) which is then optionally reacted with one or more conjugated diene hydrocarbons, one or more alkenylsubstituted aromatic compounds, or mixtures of one or more dienes with one or more alkenylaromatic compounds, in a predominantly alkane or cycloalkane reaction solvent, which solvent contains 5 to 10 carbon atoms, and mixtures of such solvents to produce a protected initiator with an extended chain  $-Q_n-Z-$  between the metal atom (Li) and element (T) in formula (I) above and mixtures thereof with compounds of formula VII.

While "A" in the protecting group  $(AR^1R^2R^3)$  of the formulae above can be any of the elements in Group IVa of the Periodic Table of the Elements, carbon and silicon initially appear to be the most useful, especially when polymerizing conjugated dienes.

The tertiary amino-1-haloalkanes useful in practicing this invention are compounds of the following general structures:



and



wherein X is defined as a halogen, preferably chlorine or bromine; Z is defined as a branched or straight chain hydrocarbon connecting group which contains 3-25 carbon atoms; A is an element selected from Group IVa of the Periodic Table of the Elements,  $R^1$ ,  $R^2$ , and  $R^3$  are independently

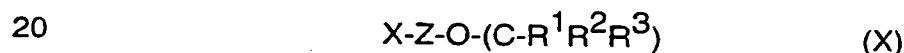
defined as hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms, and m is an integer from 1 to 7. The process reacts selected omega-tertiary-amino-1-haloalkanes whose alkyl groups contain 3 to 25 carbon atoms, with lithium metal at a temperature between about 35 °C and about 130 °C, preferably at the reflux temperature of an alkane, cycloalkane, or aromatic reaction solvent containing 5 to 10 carbon atoms and mixtures of such solvents.

Anionic polymerizations employing the tertiary amine initiators are conducted in an inert solvent, preferably a non-polar solvent, optionally containing an ethereal modifier, using an olefinic monomer which is an alkenylaromatic or a 1,3-diene at a temperature of about -30 °C to about +150 °C. The polymerization reaction proceeds from initiation to propagation to linking and is finally terminated with appropriate reagents. The multi-arm or star polymer arms before coupling with a polyfunctional linking agent, may have a molecular weight range of about 1000 to 40,000 but the molecular weight can be higher. Typically 5 to 50 milli-moles of initiator is used per mole of monomer.

Tertiary amino-1-haloalkanes useful in the practice of this invention include but are not limited to 3-(N,N-dimethylamino)-1-propyl halide, 3-(N,N-dimethylamino)-2-methyl-1-propyl halide, 3-(N,N-dimethylamino)-2,2-dimethyl-1-propyl halide, 4-(N,N-dimethylamino)-1-butyl halide, 5-(N,N-dimethylamino)-1-pentyl halide, 6-(N,N-dimethylamino)-1-hexyl halide, 3-(N,N-diethylamino)-1-propyl halide, 3-(N,N-diethylamino)-2-methyl-1-propyl halide, 3-(N,N-diethylamino)-2,2-dimethyl-1-propyl halide, 4-(N,N-diethylamino)-1-butyl halide, 5-(N,N-diethylamino)-1-pentyl halide, 6-(N,N-diethylamino)-1-hexyl halide, 3-(N-ethyl-N-methylamino)-1-propyl halide, 3-(N-ethyl-N-methylamino)-2-methyl-1-propyl halide, 3-(N-ethyl-N-methylamino)-2,2-dimethyl-1-propyl halide, 4-(N-ethyl-N-methylamino)-1-

butyl halide, 5-(N-ethyl-N-methylamino)-1-pentyl halide, 6-(N-ethyl-N-methylamino)-1-hexyl halide, 3-(piperidino)-1-propyl halide, 3-(piperidino)-2-methyl-1-propyl halide, 3-(piperidino)-2,2-dimethyl-1-propyl halide, 4-(piperidino)-1-butyl halide, 5-(piperidino)-1-pentyl halide, 6-(piperidino)-1-hexyl halide, 3-(pyrrolidino)-1-propyl halide, 3-(pyrrolidino)-2-methyl-1-propyl halide, 3-(pyrrolidino)-2,2-dimethyl-1-propyl halide, 4-(pyrrolidino)-1-butyl halide, 5-(pyrrolidino)-1-pentyl halide, 6-(pyrrolidino)-1-hexyl halide, 3-(hexamethyleneimino)-1-propyl halide, 3-(hexamethyleneimino)-2-methyl-1-propyl halide, 3-(hexamethyleneimino)-2,2-dimethyl-1-propyl halide, 4-(hexamethyleneimino)-1-butyl halide, 5-(hexamethyleneimino)-1-pentyl halide, 6-(hexamethyleneimino)-1-hexyl halide, 3-(N-isopropyl-N-methyl)-1-propyl halide, 2-(N-isopropyl-N-methyl)-2-methyl-1-propyl halide, 3-(N-isopropyl-N-methyl)-2,2-dimethyl-1-propyl halide, and 4-(N-isopropyl-N-methyl)-1-butyl halide. The halo- or halide group is selected from chlorine and bromine.

Omega-hydroxy-protected-1-haloalkanes, useful in producing the protected functional organolithium ether initiators useful in practicing this invention, have the following general structure:



wherein X is defined as a halogen, preferably chlorine or bromine; Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms,  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are independently defined as hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms. The process reacts selected omega-hydroxy-protected-1-haloalkanes whose alkyl groups contain 3 to 25 carbon atoms, with lithium metal at a temperature between about 35 °C and about 130 °C, preferably at the reflux temperature of an



alkane, cycloalkane, or aromatic reaction solvent containing 5 to 10 carbon atoms and mixtures of such solvents.

Anionic polymerizations employing the monofunctional ether initiators are conducted in an inert solvent, preferably a non-polar solvent, optionally  
5 containing an ethereal modifier, using an olefinic monomer which is an alkenylaromatic or a 1,3-diene at a temperature of about -30 °C to about +150 °C. The polymerization reaction proceeds from initiation to propagation to linking and is finally terminated with appropriate reagents. The star polymer arms, before coupling with a polyfunctional linking agent,  
10 may have a molecular weight range of about 1000 to 40,000 but the molecular weight can be higher. Typically 5 to 50 milli-moles of initiator is used per mole of monomer.

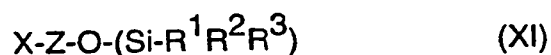
The precursor omega-protected-1-haloalkanes (halides) were prepared from the corresponding haloalcohol by the standard literature  
15 methods. For example, 3-(1,1-dimethylethoxy)-1-chloropropane was synthesized by the reaction of 3-chloro-1-propanol with 2-methylpropene according to the method of A. Alexakis, M. Gardette, and S. Colin, Tetrahedron Letters, 29, 1988, 2951. The method of B. Figadere, X. Franck and A. Cave, Tetrahedron Letters, 34, 1993, 5893, which involved the  
20 reaction of the appropriate alcohol with 2-methyl-2-butene catalyzed by boron trifluoride etherate is employed for the preparation of the t-amyl ethers. The alkoxy, alkylthio or dialkylamino substituted ethers, for example 6-[3-(methylthio)-1-propyloxy]-1-chlorohexane, were synthesized by reaction of the corresponding substituted alcohol, for instance 3-methylthio-1-  
25 propanol, with an alpha-bromo-omega-chloroalkane, for instance 1-bromo-6-hexane, according to the method of J. Almena, F. Foubelo and M. Yus, Tetrahedron, 51, 1995, 11883. The compound 4-(methoxy)-1-chlorobutane, and the higher analogs, were synthesized by the ring opening reaction of tetrahydrofuran with thionyl chloride and methanol, according to the  
30 procedure of T. Ferrari and P. Vogel, SYNLETT, 1991, 233. The triphenylmethyl protected compounds, for example 3-(triphenylmethoxy)-1-

chloropropane, are prepared by the reaction of the haloalcohol with triphenylmethylchloride, according to the method of S. K. Chaudhary and O. Hernandez, Tetrahedron Letters, 1979, 95.

Omega-hydroxy-protected-1-haloalkanes prepared in accord with this  
5 earlier process useful in practicing this invention can include, but are not limited to, 3-(1,1-dimethylethoxy)-1-propyl halide, 3-(1,1-dimethylethoxy)-2-methyl-1-propyl halide, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyl halide, 4-(1,1-dimethylethoxy)-1-butyl halide, 5-(1,1-dimethylethoxy)-1-pentyl halide, 6-(1,1-dimethylethoxy)-1-hexyl halide, 8-(1,1-dimethylethoxy)-1-octyl halide,  
10 3-(1,1-dimethylpropoxy)-1-propyl halide, 3-(1,1-dimethylpropoxy)-2-methyl-1-propyl halide, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyl halide, 4-(1,1-dimethylpropoxy)-1-butyl halide, 5-(1,1-dimethylpropoxy)-1-pentyl halide, 6-(1,1-dimethylpropoxy)-1-hexyl halide, 8-(1,1-dimethylpropoxy)-1-octyl halide, 4-(methoxy)-1-butyl halide, 4-(ethoxy)-1-butyl halide, 4-(propyloxy)-1-butyl  
15 halide, 4-(1-methylethoxy)-1-butyl halide, 3-(triphenylmethoxy)-2,2-dimethyl-1-propyl halide, 4-(triphenylmethoxy)-1-butyl halide, 3-[3-(dimethylamino)-1-propyloxy]-1-propyl halide, 3-[2-(dimethylamino)-1-ethoxy]-1-propyl halide, 3-[2-(diethylamino)-1-ethoxy]-1-propyl halide, 3-[2-(diisopropylamino)-1-ethoxy]-1-propyl halide, 3-[2-(1-piperidino)-1-ethoxy]-1-propyl halide, 3-[2-(1-pyrrolidino)-1-ethoxy]-1-propyl halide, 4-[3-(dimethylamino)-1-propyloxy]-1-butyl  
20 halide, 6-[2-(1-piperidino)-1-ethoxy]-1-hexyl halide, 3-[2-(methoxy)-1-ethoxy]-1-propyl halide, 3-[2-(ethoxy)-1-ethoxy]-1-propyl halide, 4-[2-(methoxy)-1-ethoxy]-1-butyl halide, 5-[2-(ethoxy)-1-ethoxy]-1-pentyl halide, 3-[3-(methylthio)-1-propyloxy]-1-propyl halide, 3-[4-(methylthio)-1-butyloxy]-  
25 1-propyl halide, 3-(methylthiomethoxy)-1-propyl halide, 6-[3-(methylthio)-1-propyloxy]-1-hexyl halide, 3-[4-(methoxy)-benzyloxy]-1-propyl halide, 3-[4-(1,1-dimethylethoxy)-benzyloxy]-1-propyl halide, 3-[2,4-(dimethoxy)-benzyloxy]-1-propyl halide, 8-[4-(methoxy)-benzyloxy]-1-octyl halide, 4-[4-(methylthio)-benzyloxy]-1-butyl halide, 3-[4-(dimethylamino)-benzyloxy]-1-propyl  
30 halide, 6-[4-(dimethylamino)-benzyloxy]-1-hexyl halide, 5-(triphenylmethoxy)-1-pentyl halide, 6-(triphenylmethoxy)-1-hexyl halide, and

8-(triphenylmethoxy)-1-octyl halide. The halo- or halide group is selected from chlorine and bromine.

U.S. Patent 5,362,699 discloses a process for the preparation of hydrocarbon solutions of monofunctional ether initiators derived from  
5 omega-hydroxy-silyl-protected-1-haloalkanes of the following general structure:

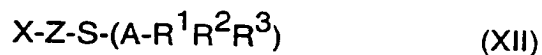


10 wherein X is defined as a halogen, preferably chlorine or bromine; Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups; and R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are independently defined as saturated and unsaturated aliphatic and aromatic radicals, and their employment as initiators in the anionic  
15 polymerization of olefin containing monomers in an inert, hydrocarbon solvent optionally containing a Lewis base. The process reacts selected omega-hydroxy-protected-1-haloalkanes whose alkyl groups contain 3 to 25 carbon atoms, with lithium metal at a temperature between about 25 °C and about 40 °C, in an alkane, cycloalkane or aromatic reaction solvent  
20 containing 5 to 10 carbon atoms and mixtures of such solvents.

Anionic polymerizations employing the monofunctional silyl ether initiators are conducted in an inert solvent, preferably a non-polar solvent, optionally containing an ethereal modifier, using an olefinic monomer which is an alkenylaromatic or a 1,3-diene at a temperature of about -30 °C to  
25 about +150 °C. The polymerization reaction proceeds from initiation to propagation to linking and is finally terminated with appropriate reagents. The star polymer arms, before coupling with a multifunctional linking agent, may have a molecular weight range of about 1000 to 40,000 but the molecular weight can be higher. Typically 5 to 50 milli-moles of initiator is  
30 used per mole of monomer.

Omega-silyloxy-1-haloalkanes prepared in accord with this earlier process useful in practicing this invention can include, but are not limited to, 3-(t-butyldimethylsilyloxy)-1-propyl halide, 3-(t-butyldimethyl-silyloxy)-2-methyl-1-propyl halide, 3-(t-butyldimethylsilyloxy)-2,2-dimethyl-1-propyl  
 5 halide, 4-(t-butyldimethylsilyloxy)-1-butyl halide, 5-(t-butyldimethyl-silyloxy)-1-pentyl halide, 6-(t-butyldimethylsilyloxy)-1-hexyl halide, 8-(t-butyldimethylsilyloxy)-1-octyl halide, 3-(t-butyldiphenylsilyloxy)-1-propyl halide, 3-(t-butyldiphenylsilyloxy)-2-methyl-1-propyl halide, 3-(t-butyldiphenylsilyloxy)-2,2-dimethyl-1-propyl halide, 6-(t-  
 10 butyldimethylsilyloxy)-1-hexyl halide, and 3-(trimethylsilyloxy)-2,2-dimethyl-1-propyl halide. The halo- or halide group is selected from chlorine and bromine.

Monofunctional thioether initiators useful in the practice of this invention are derived from omega-thio-protected-1-haloalkanes of the  
 15 following general structure:



wherein X is defined as a halogen, preferably chlorine or bromine; Z is a  
 20 branched or straight chain hydrocarbon group which contains 3-25 carbon atoms;  $(A-R^1R^2R^3)$  is a protecting group in which A is an element selected from Group IVa of the Periodic Table of the Elements;  $R^1$ ,  $R^2$ , and  $R^3$  are independently defined as hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or  
 25 substituted aryl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms. The process reacts selected omega-thioprotected-1-haloalkyls whose alkyl groups contain 3 to 25 carbon atoms, with lithium metal at a temperature between about 35 °C and about 130 °C,  
 30 preferably at the reflux temperature of an alkane, cycloalkane or aromatic

reaction solvent containing 5 to 10 carbon atoms and mixtures of such solvents.

Anionic polymerizations employing the monofunctional thio ether initiators are conducted in an inert solvent, preferably a non-polar solvent, optionally containing an ethereal modifier, using an olefinic monomer which is an alkenylaromatic or a 1,3-diene at a temperature of about -30 °C to about +150 °C. The polymerization reaction proceeds from initiation to propagation to linking and is finally terminated with appropriate reagents. The polymer before coupling with a polyfunctional linking agent, may have a molecular weight range of about 1000 to 40,000 but the molecular weight can be higher. Typically 5 to 50 milli-moles of initiator is used per mole of monomer.

The initiator precursor, omega-thio-protected-1-haloalkanes (halides), are prepared from the corresponding halothiol by the standard literature methods. For example, 3-(1,1-dimethylethylthio)-1-propylchloride is synthesized by the reaction of 3-chloro-1-propanthiol with 2-methylpropene according to the method of A. Alexakis, M. Gardette, and S. Colin, *Tetrahedron Letters*, 29, 1988, 2951. Alternatively, reaction of 1,1-dimethylethylthiol with 1-bromo-3-chloropropane and a base affords 3-(1,1-dimethylethylthio)-1-propylchloride. The method of B. Figadere, X. Franck and A. Cave, *Tetrahedron Letters*, 34, 1993, 5893, which involved the reaction of the appropriate thiol with 2-methyl-2-butene catalyzed by boron trifluoride etherate is employed for the preparation of the t-amyl ethers. Additionally, 5-(cyclohexylthio)-1-pentylhalide and the like, can be prepared by the method of J. Almena, F. Foubelo, and M. Yus, *Tetrahedron*, 51, 1995, 11883. This synthesis involves the reaction of the appropriate thiol with an alkyl lithium, then reaction of the lithium salt with the corresponding alpha, omega dihalide. 3-(Methylthio)-1-propylchloride can be prepared by chlorination of the corresponding alcohol with thionyl chloride, as taught by D. F. Taber and Y. Wang, *J. Org. Chem.*, 58, 1993, 6470. Methoxymethylthio compounds, such as 6-(methoxymethylthio)-1-

hexylchloride, are prepared by the reaction of the omega-chloro-thiol with bromochloromethane, methanol, and potassium hydroxide, by the method of F. D. Toste and I. W. J. Still, Synlett, 1995, 159. t-Butyldimethylsilyl protected compounds, for example 4-(t-butyldimethylsilylthio)-1-butylhalide, are prepared from t-butyldimethylchlorosilane, and the corresponding thiol, according to the method described in U. S. Patent No. 5,493,044.

Omega-thio-protected 1-haloalkanes prepared in accord with this earlier process useful in practicing this invention can include, but are not limited to, 3-(methylthio)-1-propylhalide, 3-(methylthio)-2-methyl-1-propylhalide, 3-(methylthio)-2,2-dimethyl-1-propylhalide, 4-(methylthio)-1-butylhalide, 5-(methylthio)-1-pentylhalide, 6-(methylthio)-1-hexylhalide, 8-(methylthio)-1-octylhalide, 3-(methoxymethylthio)-1-propylhalide, 3-(methoxymethylthio)-2-methyl-1-propylhalide, 3-(methoxymethylthio)-2,2-dimethyl-1-propylhalide, 4-(methoxymethylthio)-1-butylhalide, 5-(methoxymethylthio)-1-pentylhalide, 6-(methoxymethylthio)-1-hexylhalide, 8-(methoxymethylthio)-1-octylhalide, 3-(1,1-dimethylethylthio)-1-propylhalide, 3-(1,1-dimethylethylthio)-2-methyl-1-propylhalide, 3-(1,1-dimethylethylthio)-2,2-dimethyl-1-propylhalide, 4-(1,1-dimethylethylthio)-1-butylhalide, 5-(1,1-dimethylethylthio)-1-pentylhalide, 6-(1,1-dimethylethylthio)-1-hexylhalide, 8-(1,1-dimethylethylthio)-1-octylhalide, 3-(1,1-dimethylpropylthio)-1-propylhalide, 3-(1,1-dimethylpropylthio)-2-methyl-1-propylhalide, 3-(1,1-dimethylpropylthio)-2,2-dimethyl-1-propylhalide, 4-(1,1-dimethylpropylthio)-1-butylhalide, 5-(1,1-dimethylpropylthio)-1-pentylhalide, 6-(1,1-dimethylpropylthio)-1-hexylhalide, 8-(1,1-dimethylpropylthio)-1-octylhalide, 3-(cyclopentylthio)-1-propylhalide, 3-(cyclopentylthio)-2-methyl-1-propylhalide, 3-(cyclopentylthio)-2,2-dimethyl-1-propylhalide, 4-(cyclopentylthio)-1-butylhalide, 5-(cyclopentylthio)-1-pentylhalide, 6-(cyclopentylthio)-1-hexylhalide, 8-(cyclopentylthio)-1-octylhalide, 3-(cyclohexylthio)-1-propylhalide, 3-(cyclohexylthio)-2-methyl-1-propylhalide, 3-(cyclohexylthio)-2,2-dimethyl-1-propylhalide, 4-(cyclohexylthio)-1-butylhalide, 5-(cyclohexylthio)-1-pentylhalide, 6-(cyclohexylthio)-1-hexylhalide, 8-

(cyclohexylthio)-1-octylhalide, 3-(t-butyltrimethylsilylthio)-1-propylhalide, 3-(t-butyltrimethylsilylthio)-2-methyl-1-propylhalide, 3-(t-butyltrimethylsilylthio)-2,2-dimethyl-1-propylhalide, 3-(t-butyltrimethylsilylthio)-2-methyl-1-propylhalide, 4-(t-butyltrimethylsilylthio)-1-butylhalide, 6-(t-butyltrimethylsilylthio)-1-hexylhalide and 3-(trimethylsilylthio)-2,2-dimethyl-1-propylhalide. The halo- or halide group is selected from chlorine and bromine.

M is a monomer selected from the group of conjugated alkadienes, such as butadiene and isoprene, and alkenylaromatic compounds such as styrene and alpha-methylstyrene. The dienes may be polymerised alone, or in admixture with each other or with alkenylsubstituted aromatic compounds to form random copolymers, or by charging the dienes to the reaction mixture sequentially, either with each other or with alkenylsubstituted aromatic compounds, to form block copolymers. Examples of conjugated diene hydrocarbons include, but are not limited to: 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, myrcene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 1,3-heptadiene, 3-methyl-1,3-heptadiene, 1,3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene, 3-n-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, 2,4-diethyl-1,3-butadiene, 2,3-di-n-propyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, and myrcene.

Examples of polymerizable alkenylsubstituted aromatic compounds which can be anionically polymerized include, but are not limited to: styrene, alpha-methylstyrene, vinyltoluene, 2-vinylpyridine, 4-vinylpyridine, 1-vinylnaphthalene, 2-vinylnaphthalene, 1-alpha-methylvinyl-naphthalene, 2-alpha-methylvinyl-naphthalene, 1,2-diphenyl-4-methylhexene-1 and mixtures of these, as well as alkyl, cycloalkyl, aryl, alkaryl and aralkyl derivatives thereof in which the total number of carbon atoms in the combined hydrocarbon constituents is generally not greater than 18. Examples of these latter compounds include; 3-methylstyrene, 3,5-diethylstyrene, 2-ethyl-4-benzylstyrene, 4-phenylstyrene, 4-p-tolylstyrene, 4-

(tert-butyl)-styrene, 2,4-divinyltoluene and 4,5-dimethyl-1-vinylnaphthalene. Reference is made to U. S. Patent No. 3,377,404 for disclosures of additional alkenyl substituted aromatic compounds.

5        Examples of linking or coupling agents recommended to link the  
polymer anions produced in the polymerizations initiated by the protected  
functional initiators are tri- and tetrahalosilanes, polyhalodisilanes, and tri-  
haloalkylsilanes, polyhaloalkyldisilanes, tri-, and tetrahalostannanes, and  
tri-haloalkylstannanes, 1,2, 1,3, and 1,4-divinylbenzene, 1,2, 1,3, and 1,4-  
diisopropenylbenzene, 1,2,4-trivinylbenzene, 1,3-divinylnaphthalene, 1,8-  
10    divinylnaphthalene, 1,3,5-trivinylbenzene, 1,3,5-tris(1-  
phenylethenyl)benzene and other materials known in the art to be useful for  
linking or coupling of polymers. See for example, U. S. Patent No.  
5,489,649 for additional linking agents. Of course, mixtures of the linking  
agents may also be employed. The amount of linking agent added is such  
15    that the molar ratio of protected living polymer anions to linking agent is in  
the range of 1 to 24.

      The reaction medium is generally an inert solvent, typically a non-  
polar solvent such as a hydrocarbon, since anionic polymerization in the  
presence of such non-polar solvents is known to produce polydienes with  
20    high 1,4-contents from 1,3-dienes. Inert hydrocarbon solvents useful in  
practicing this invention include but are not limited to inert liquid alkanes,  
cycloalkanes and aromatic solvents such as alkanes and cycloalkanes  
containing five to ten carbon atoms such as pentane, hexane,  
cyclohexane, methylcyclohexane, heptane, methylcycloheptane, octane,  
25    decane and so forth and aromatic solvents containing six to ten carbon  
atoms such as toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, n-  
propylbenzene, isopropylbenzene, n-butylbenzene, t-butylbenzene, and  
the like.

      Polar solvents (modifiers) can be added to the polymerization  
30    reaction to alter the microstructure of the resulting polymer, i.e., increase the  
proportion of 1,2 (vinyl) microstructure or to promote functionalization or



randomization, in the case of copolymerization. Examples of polar modifiers include, but are not limited to: diethyl ether, dibutyl ether, tetrahydrofuran, 2-methyltetrahydrofuran, methyl tert-butyl ether, alkali metal alkoxides, diazabicyclo[2.2.2]octane, triethylamine, tributylamine, 5 tetramethylethylene diamine (TMEDA), and 1,2-dimethoxyethane (glyme). The amount of the polar modifier added depends on the vinyl content desired, the nature of the monomer, the temperature of the polymerization, and the identity of the polar modifier. The polar solvent (modifier) can be added to the reaction medium at the beginning of the polymerization as part 10 of the solvent reaction medium or added during the polymerization.

After reaction of the protected living polymer anion with the polyfunctional coupling agents, the reaction may be terminated by the addition of a proton donor, such as water, methanol, isopropanol, octanol, or acetic acid. The resultant multi-arm polymer may then be isolated by 15 conventional means. For example, the reaction mixture may be poured into a precipitant, such as isopropanol to precipitate the polymer, followed by filtration and drying of the polymer. Alternatively, after termination, the solvent may be removed, to afford the protected multi-arm polymer.

If desired, the protecting groups can be removed from the arms of the 20 multi-arm or star polymer to produce other novel polymers which can be reacted with a number of other comonomers to produce yet another group of novel block polymers. These multi-arm or star polymers with terminal functional groups at the ends of the arms can be classified as "multichelic" or telechelic multi-arm polymers, analogous to alpha, omega difunctionally 25 terminated linear polymers, which are typically called "telechelic" polymers. Typically employed comonomer formulas which can be polymerized with the selectively deprotected multichelically functional multi-arm or star polymers of this invention are bisphenol A and phosgene, caprolactam and adipic acid, hexamethylene diamine and adipic acid, dimethyl terephthalate and 30 1,4-butanediol, and diphenyl methane diisocyanate and 1,4-butanediol, which produce, respectively, blocks of polycarbonate, polyamide, polyester,

and polyurethane attached to the selectively deprotected telechelically functional polydiene, polyarylethylene, or polydiene/polyarylethylene arms of the star polymer. Where acid catalysis of such copolymerizations is employed, for example when the comonomer is a mixture of caprolactam and adipic acid and the catalyst is 85% phosphoric acid (aq) one may expect simultaneous deprotection of t-butyldimethylsilyl protecting groups to occur. Block arm lengths, as well as the nature of the blocks themselves, can be varied during copolymerization to allow for the preparation of a wide spectrum of multichelic segmented block star or multi-arm copolymers.

These products find utility in coatings, binders, sealants, and molding resins. Reference is made to U.S. Patents 4,994,526 and 5,393,843 for further details of the copolymerizations.

The deprotection step can be performed either prior to or after the optional hydrogenation of the residual unsaturation of the arms. For example, to remove tert-alkyl-protecting groups, the protected polymer is mixed with Amberlyst® 15 ion exchange resin and heated at an elevated temperature, for example 150 °C, or at the reflux temperature of the solvent (cyclohexane) until deprotection is complete. In addition, tert-alkyl-protecting groups can also be removed by reaction of the star polymer with trifluoroacetic acid, p-toluenesulfonic acid, or trimethylsilyliodide. Additional methods of deprotection of the tert-alkyl protecting groups can be found in T.W. Greene and P.G.M. Wuts, Protective Groups in Organic Synthesis, Second Edition, Wiley, New York, 1991, page 41. The tert-butyldimethylsilyl protecting groups can be removed by treatment of the multi-arm or star polymer with acid, such as hydrochloric acid, acetic acid, para-toluenesulfonic acid, or Dowex® 50W-X8. Alternatively, a source of fluoride ions, for instance tetra-n-butylammonium fluoride, potassium fluoride and 18-crown-6, or pyridine-hydrofluoric acid complex, can be employed for removal of the tert-butyldimethylsilyl protecting groups. Additional methods of removal of the tert-butyldimethylsilyl protecting groups can be found in

T.W. Greene and P.G.M. Wuts, Protective Groups in Organic Synthesis, Second Edition, Wiley, New York, 1991, pages 80-83.

Examples of methods to hydrogenate the polymers of this invention are described in U. S. Patent Nos. 4,970,254, 5,166,277, 5,393,843 and  
5 5,496,898. The hydrogenation of the multi-arm or star polymer is conducted in situ, or in a suitable solvent, such as hexane, cyclohexane or heptane. This solution is contacted with hydrogen gas in the presence of a catalyst, such as a nickel catalyst. The hydrogenation is typically performed at temperatures from 25 °C to 150 °C, with a archetypal hydrogen pressure of  
10 15 psig to 1000 psig. The progress of this hydrogenation can be monitored by InfraRed (IR) spectroscopy or Nuclear Magnetic Resonance (NMR) spectroscopy. The hydrogenation reaction is conducted until at least 90% of the aliphatic unsaturation has been saturated. The hydrogenated star or multi-arm polymer is then recovered by conventional procedures, such as  
15 removal of the catalyst with aqueous acid wash, followed by solvent removal or precipitation of the polymer.

The protected hydroxy multi-arm star polymers of this invention alone and in their hydrogenated forms, could be used as base materials to lend flexibility and higher impact strength in a number of formulas to produce  
20 coatings, sealants, binders and block copolymers with polyesters, polyamides and polycarbonates as described in UK Patent Application GB2)70317A and in "Polytail" data sheets and brochures (Mitsubishi Kasei America).

Thus, in the presence of acidic catalysts used to promote the  
25 formation of many of these block copolymer resins, the protective group of the hydrogenated polymer is removed as well, allowing the exposed hydroxyl grouping in the base polymer molecule to simultaneously participate in the block copolymer reaction.

The multi-arm or star, segmented block copolymer which results, will be a  
30 segmented-linear, star-branched, or network polymer depending on the degree of functionality of the stars.

A segmented polyester-hydrogenated multi-arm block copolymer can be so produced by reaction of hydrogenated multi-arm polymer with dimethyl terephthalate and a suitable acidic catalyst. Again, the products are useful as molding compounds for exterior automotive components.

5           A segmented polyamide-hydrogenated block copolymer is useful as a molding composition to prepare exterior automotive components that can be prepared by reacting hydrogenated multi-arm polymer with caprolactam and adipic acid in the presence of a suitable catalyst.

          Isocyanate-terminated prepolymers can be produced from  
10 hydrogenated multi-arm hydroxyfunctional polymers by reaction with suitable diisocyanates (2/1 NCO/OH) as above and which can be further reacted with diols and additional diisocyanates to form segmented polyurethanes useful for water based, low VOC coatings. Inclusion of acid functional diols such as dimethylolpropionic acid in the polyurethane introduces pendant  
15 carboxyl groups which can be neutralized with tertiary amines to afford water dispersable polyolefin/polyurethane segmented stars for water based coatings. This same principle could be applied to acrylic polymers made with tertiary amine functional monomers included, which could be made by free radical polymerization following reacting the hydroxyl groups at the  
20 terminal ends of the star with acryloyl chloride or methacryloyl chloride. Or segmented polyurethane prepolymers may be mixed with tackifying resins and used as a moisture-curable sealant, caulk or coating.

          Alternatively, the protecting groups may be removed, either before or after hydrogenation of the aliphatic unsaturation, then the hydroxy  
25 terminated multi-arm polymer may be reacted with functional comonomers, to produce novel copolymers. Thus, for example, the hydroxy terminated polymer may be hydrogenated, and then reacted with ethylene oxide in the presence of potassium tert-butoxide to produce a poly(ethyleneoxide)-hydrogenated star block copolymer. This reaction sequence affords a  
30 hydrogel.

Further, after deprotection has been achieved using acid catalysis, hydrogenated multi-arm hydroxyterminated polymers may be reacted with bisphenol A and phosgene in the presence of appropriate basic catalysts to yield a polycarbonate block copolymer. The resulting products are useful  
5 as molding resins, for example, to prepare interior components for automobiles.

Another application for the hydroxyfunctional multi-arm or star polymer in coatings is in the preparation of new dendrimers, based on the use of the polymer in its hydrogenated or  
10 unhydrogenated form as the base core for dendritic hybrid macromolecules derived by condensation or addition polymerizations utilizing the hydroxyl functionality as the initiating site (see, for example Gitsov and Frechet, American Chemical Society PMSE Preprints, Volume 73, August 1995).

The polar functional groups on the polymer chain ends allow the polymers of this  
15 invention to alter the surface properties of polymers like polyethylene and polypropylene. When the polymers of this invention are blended with non-polar polyolefins, the polar functional groups on the chain ends, being incompatible with the non-polar polyolefin, will phase separate and migrate to the surface of the polyolefin. Properties such as surface adhesion are thus greatly enhanced, leading to improved  
20 adhesion of pigments in printing inks for labels, composite layering, and other adhesive applications. An alternative approach to modification of polymer surfaces to alter properties by introduction of functional groups has been the use of chemical reagents such as alkylolithiums ( see, for example, A.J. Dias, K-W Lee, and T.J. McCarthy, Rubber & Plastics News, 18-20, October 31, 1988, and A.J. Dias and T.J. McCarthy,  
25 Macromolecules, 20, 1437 (1987)).

Yet another application for these telechelic functionalized multi-arm or star polymers would be for new toughening polymers for epoxy composites, utilizing the elastomer diene core with the hydroxyl groups converted to half esters by reaction with anhydrides, or converted to anhydrides by reaction  
30 with a halo-functional anhydride such as trimellitic anhydride chloride. . These epoxy reactive stars can then be utilized as reactants with epoxy

resins and amines in such composite systems. Reacting the hydroxyl functional stars into unsaturated polyesters provides a new polymer toughening system for polyester molding compounds for automotive and other uses. For a review of the use of linear polymers for toughening of epoxies and polyesters, see "Rubber-Toughened Plastics", Edited By  
5 C.Keith Riew, ACS Advances in Chemistry Series ,#222.

Cathodic electrodepositable coatings may be prepared from the epoxy functional multi-arm or star polymers described above by reacting with epoxy resins in the presence of excess amine or polyamine, to  
10 completely react all the epoxy groups, distilling off the excess amine, and neutralizing the resulting epoxy- amine adduct with water soluble organic or inorganic acids to form water soluble, quarternary ammonium containing polymer salts (see for reference, U. S. Patents 3,617,458, 3,619,398, 3,682,814, 3,891,527, 3,947,348, and 4,093,594). Alternatively, the above  
15 epoxy-amine polymer star adducts may be converted to quarternary phosphonium, or sulfonium ion containing polymers as in U. S. Patent 3,935,087.

In another application, the deprotected polymer may be reacted with chloromethylstyrene, or with an alkenylarylhalosilane such as  
20 styrenyldimethylchlorosilane to yield the corresponding omega-styrenylterminated macromonomer according to directions in US 5,278,244 which may then be further polymerized by a variety of techniques to yield heterophase polymer network systems.

In still another application, the hydrogenated hydroxyterminated  
25 branches of the star polymer may be further reacted with acryloyl chloride or methacryloyl chloride, and the resultant acrylate or methacrylate-terminated polymer further polymerized with monomers selected from the group of alkyl acrylates, alkyl methacrylates, hydroxyallyl methacrylates, and dialkylacrylamides to produce hydrogels. Further, the acrylate or  
30 methacrylate-terminated multi-arm polymer may be polymerized by free-radical processes.

An acrylate-terminated prepolymer curable by free-radical processes can be prepared from the hydrogenated multi-arm hydroxyfunctional polymer by reaction with a diisocyanate (2NCO/OH) followed by further reaction with hydroxyethyl acrylate in the presence of a basic reagent.

5           V.I. Improvers is another likely application for this acrylate or methacrylate terminated polymer, where by using carboxyl functional monomers such as acrylic acid and methacrylic acid and /or amine functional monomers such as acrylamide along with free radical initiators in further polymerizations, the result is formation of polymer segments at the  
10 periphery of each star arm with amine or other functionalities which, in addition to the advantageous properties of the star polymers for V.I. Improvers, combines the ability to add functionality to the arms for dispersant properties (see for example, U.S. Patents 5,496,898, 4,575,530, 4,486,573, 5,290,874, and 5,290,868).

15           The versatility of the hydroxyl functional multi-arm or star polymers of this invention, and the wide range of different segmented polymers (polyethers, polyesters, polyamides, polycarbonates, polyurethanes, etc.) which can be initiated at the hydroxyl groups, leads to numerous possible applications as compatibilizers for polymer blends and alloys. In addition to  
20 the use of such blends for new applications, much recent interest is generated in the use of compatibilizers to facilitate polymer waste recycling.

          In contrast to star polymers of the prior art, the molecular architecture of compounds of the present invention can be precisely controlled. Those arms of the multi-arm polymer, which are generated from a protected  
25 functional initiator, contain a protected functional group. The nature of the functional group, and its protecting group can be varied, simply by changing the initiator. Further, the monomer identity, the monomer composition and molecular weight of the functional arms can be independently manipulated by varying the monomer charged to the initiator, as well as the ratio of  
30 functional to non-functional initiator. Finally, the number of polymer arms

can be adjusted by varying the nature of the coupling agent, and the ratio of living polymer to the coupling agent.

The following are examples of the preparation of the polymers of this invention.

### PREPARATION OF THE INITIATORS

#### Example A

Preparation of 3-(t-Butyldimethylsilyloxy)-1-propyllithium Chain  
Extended with 2 Moles of Isoprene Lot 8983 (461-68)

A 500 ml, three-necked Morton flask was equipped with a mechanical stirrer, a 125 ml. pressure-equalizing addition funnel, and a Claisen adapter fitted with a thermocouple, a reflux condenser, and an argon inlet. This apparatus was dried in an oven overnight at 125 °C, assembled hot, and allowed to cool to room temperature in a stream of argon. Lithium dispersion was washed free of mineral oil with hexane (2 X 70 ml), and pentane (1 X 70 ml), then dried in a stream of argon. The dry dispersion, 5.20 grams (0.749 mole, 2.80 equivalents) was transferred to the flask with 260 ml cyclohexane. This suspension was stirred at 450 RPMs, and heated to 65 °C with a heating mantle. The heat source was removed. 1-(t-Butyldimethylsilyloxy)-3-chloropropane, 58.82 grams (0.268 mole, 1.00 equivalent) was added dropwise. An exotherm was detected after 31.8% of the feed had been added. A dry ice/hexane cooling bath was applied to maintain the reaction temperature at 60-65 °C. The total feed time was one hundred five minutes. An exotherm was noted until the last drop of feed was added, then the temperature fell off rapidly to room temperature. The reaction mixture was stirred at room temperature for forty five minutes, then heated to 65 °C with a heating mantle. The heat source was removed. Isoprene, 36.45 grams (0.535 mole, 2.00 equivalents) was then added dropwise. An exotherm was noted after 24.6% of the feed had been added.



Hexane cooling was applied to maintain the reaction temperature at 60-65 °C. The total isoprene feed time was thirty eight minutes. The reaction mixture was allowed to stir at room temperature for one hour, then transferred to a small pressure filter with argon pressure. Very rapid  
5 filtration was observed with 2 psi argon. The muds were reslurried with cyclohexane (2 X 50 ml). This afforded an orange solution, yield = 530 ml, 425.34 grams.

Total base = 17.1 wt. %.

Active C-Li = 15.9 wt %.

10 Yield (based on active C-Li) = 80.8%.

#### Example B

Preparation of 3-(t-Butyldimethylsilylthio)-1-propyllithium Chain

Extended with 2 Moles of Isoprene Lot 12083 (761-68)

#### HYPOTHETICAL

15

A 500 ml, three-necked Morton flask is equipped with a mechanical stirrer, a 125 ml. pressure-equalizing addition funnel, and a Claisen adapter fitted with a thermocouple, a reflux condenser, and an argon inlet. This apparatus is dried in an oven overnight at 125 °C, assembled hot, and  
20 allowed to cool to room temperature in a stream of argon. Lithium dispersion is washed free of mineral oil with hexane (2 X 70 ml), and pentane (1 X 70 ml), then dried in a stream of argon. The dry dispersion, 5.20 grams (0.749 mole, 2.80 equivalents) is transferred to the flask with 260 ml cyclohexane. This suspension is stirred at 450 RPMs, and heated to  
25 65 °C with a heating mantle. The heat source is removed. 1-(t-Butyldimethylsilylthio)-3-chloro-propane, 60.22 grams (0.268 mole, 1.00 equivalent) is added dropwise. An exotherm is detected after 21.8% of the feed has been added. A dry ice/hexane cooling bath is applied to maintain the reaction temperature at 60-65 °C. The total feed time is one hundred  
30 minutes. An exotherm is noted until the last drop of feed is added, then the temperature falls off rapidly to room temperature. The reaction mixture is

stirred at room temperature for forty five minutes, then heated to 65 °C with a heating mantle. The heat source is removed. Isoprene, 36.45 grams (0.535 mole, 2.00 equivalents) is then added dropwise. An exotherm is noted after 24.6% of the feed has been added. Hexane cooling is applied to maintain the reaction temperature at 60-65 °C. The total isoprene feed time is thirty eight minutes. The reaction mixture is allowed to stir at room temperature for one hour, then transferred to a small pressure filter with argon pressure. Very rapid filtration is achieved with 2 psi argon. The muds are reslurried with cyclohexane (2 X 50 ml). This affords an orange solution; yield = 530 ml, 435.21 grams.

Total base = 17.7 wt. %.

Active C-Li = 16.9 wt %.

Yield (based on active C-Li) = 82.4%.

15

## Example C

Preparation of 3-(N,N-Dimethylamino)-1-propyllithium Chain Extended with 2 Moles of Isoprene, Lot 9314

A 500 ml, three-necked Morton flask was equipped with a mechanical stirrer, a 125 ml. pressure-equalizing addition funnel, and a Claisen adapter fitted with a thermocouple, a reflux condenser, and an argon inlet. This apparatus was dried in an oven overnight at 125° C, assembled hot, and allowed to cool to room temperature in a stream of argon. Lithium dispersion was washed free of mineral oil with hexane (2 X 70 ml), and pentane (1 X 70 ml), then dried in a stream of argon. The dry dispersion, 10.57 grams (1.520 moles) was transferred to the flask with 250 ml cyclohexane. Coarse sand, 45.3 grams, was added to the reaction mixture. This suspension was stirred at 600-675 RPMs, and heated to 37° C with a heating mantle. The heat source was removed. 1-Chloro-3-(N,N-dimethylamino)propane, 19.64 grams (0.1615 mole) dissolved in 120 ml. cyclohexane was added dropwise. An exotherm (up to 52° C) was detected

after 7% of the feed had been added. A dry ice/hexane cooling bath was applied to maintain the reaction temperature at 41-44° C. The total feed time was thirty-two minutes. An exotherm was noted until the last drop of feed was added, then the temperature was maintained at 36-40° C for an additional thirty minutes. The reaction mixture was then transferred to a sintered glass filter while still warm. The filtration was complete in three minutes with three psi argon pressure. This afforded a hazy suspension.

Yield = 400 ml., 298.2 grams.

10 Active C - Li = 0.361 M (0.469 m / kg) @ 40° C.

Yield (based on active C - Li = 87%.

The product crystallized from solution upon standing at room temperature.

The concentration of the clear supernatant solution was about 0.3 M.

15 A dry 500 ml round bottom flask was fitted with a magnetic stir bar, and an argon inlet. This apparatus was purged with argon, then 154.77 grams (0.0726 mole) of the suspension prepared above was added to the flask. Isoprene, 9.4 grams (0.138 mole, 1.90 equivalents) was then added all at once. The reaction mixture was then heated to 48-49° C for forty minutes.

20 This afforded a slightly hazy golden solution, which was partially vacuum-stripped on the rotary evaporator to afford the product solution.

Yield = 43.32 grams.

Active C - Li = 1.36 M (1.65 m / kg).

25 Recovered yield (based on active C - Li) = 98.5%.

## EXAMPLES OF THE INVENTION - PREPARATION OF POLYMERS

### EXAMPLE 1

30

#### Preparation of Protected Functional Star Polymer

A star polymer with functionalized and non-functionalized arms was produced by purging an all-glass, high vacuum reactor with dry argon and charging it with 0.273 mmol of 3-t-butoxy-1-propyllithium (0.91ml, 0.3M in toluene, chain-extended with 2 units of isoprene) and 0.273 mmol of sec-butyllithium (0.21ml, 1.3M in cyclohexane) under a positive argon pressure. Purified, dry cyclohexane (200ml) was distilled directly into the reactor followed by removal from the vacuum line by heat sealing with a hand torch. Next, the reactor was heated to 50 °C and then 10.6g (15.6ml) of isoprene was added via an attached ampoule with stirring. After heating for 5 hours at 50-55 °C, a 2ml aliquot of poly(isoprenyl)lithium was removed via a sample port, the sample port was sealed off with a hand torch, and the sample was quenched with methanol. . Analysis of the base polymer by SEC afforded  $M_n = 29,000$  g/mol. After raising the temperature to 60 °C, 0.26ml of divinylbenzene (55% purity, 0.001mol) was added to provide a [DVB]/[poly(isoprenyl)lithium] = 3. After stirring at 60 °C for 9 hours, the reaction was terminated by addition of 1.5ml of degassed methanol. The resulting polymer was precipitated into methanol two times and dried in a vacuum oven. The polymer was analyzed by SEC and by  $^1\text{H}$  NMR spectroscopy. The polymer molecular weight by SEC analysis (polyisoprene standards) corresponded to  $M_n = 450,000$  (universal calibration method) and  $M_w/M_n = 1.33$ . The amount of unlinked polyisoprene corresponded to approximately 16 wt.%. The  $^1\text{H}$  NMR spectrum of the final polymer exhibited peaks at  $\delta = 1.165$  and 0.844 ppm corresponding to the tert-butoxy and sec-butyl end groups, respectively. The resulting polymer is optionally hydrogenated.

#### EXAMPLE 2 (Hypothetical)

##### Deprotection of Functional Star Polymer Produced in Example 1

A 1.00 gram sample of the polymer prepared in Example 1 is dissolved in 10ml of toluene containing 0.5g of Amberlyst® 15 Resin. The mixture is heated at reflux for 13 hours. The reaction mixture is cooled to room temperature, the resin is removed by filtration, the solvent is removed,  
5 and the polymer is vacuum dried. The <sup>1</sup>H NMR spectrum of the polymer exhibits no peaks corresponding to the tert-butoxy end group at  $\delta = 1.17$  ppm.

### EXAMPLE 3 (Hypothetical)

#### 10 Hydrogenation of t-butoxy functionalized polyisoprene star

The hydrogenation catalyst is preformed by mixing 1.00 gram (8% in pentane) nickel octoate and 0.76 grams of triethylaluminum (25% in cyclohexane) in a small, dry vial. The final ratio of aluminum to nickel is  
15 1.22. The dry hydrogenation vessel is purged with argon, then charged with the t-butoxy substituted multi-arm polymer prepared in Example 1, purified cyclohexane, and finally, the catalyst (prepared above). The atmosphere is exchanged with hydrogen gas by pressuring the vessel up to 20 psi, and then releasing the pressure. This is repeated 5 times. The pressure is then  
20 increased to 90 psi, and the magnetically stirred solution is then heated to 70 °C. The hydrogenation is conducted for twelve hours. The reaction mixture is then allowed to cool to room temperature, and the hydrogen pressure is released. The catalyst is removed by washing the polymer with dilute acid (0.5% hydrochloric acid) three times. The polymer is recovered  
25 and dried.

The resultant saturated functionalized star polymer was fully characterized by <sup>1</sup>H NMR, IR and SEC, and had the following properties:

Mn = 430,000 g/mole (based on universal calibration method).

30 <sup>1</sup>H NMR indicates that all the aliphatic unsaturation (4.50-5.20 ppm) is consumed, and that the t-butoxy group is still present (1.15 ppm).

IR indicates all the aliphatic double bond absorptions at 800-900 and 1650-1670 wavenumbers are gone.

5

#### EXAMPLE 4 (Hypothetical)

##### Deprotection of Hydrogenated Functional Star Polymer Produced in Example 3

10

A 1.00 gram sample of the polymer prepared in Example 3 is dissolved in 10ml of toluene containing 0.5g of Amberlyst® 15 Resin. The mixture is heated at reflux for 13 hours. The reaction mixture is cooled to room temperature, the resin is removed by filtration, the solvent is removed, and the polymer is vacuum dried. The <sup>1</sup>H NMR spectrum of the polymer exhibits no peaks corresponding to the tert-butoxy end group at  $\delta = 1.17$  ppm.

15

#### EXAMPLE 5 (Hypothetical)

20

##### Preparation of Protected Functionalized Star Molecule

A star polymer with functionalized and non-functionalized arms is produced by purging an all-glass, high vacuum reactor with dry argon and charging it with 0.511 mmol of 3-(t-butyltrimethylsilyloxy)-1-propyllithium (0.73 ml, 0.7M in cyclohexane) and 0.511 mmol of n-butyllithium (0.25 ml, 2.0 M in cyclohexane) under a positive argon pressure. Purified, dry cyclohexane (400ml) is distilled directly into the reactor followed by removal from the vacuum line by heat sealing with a hand torch. Next, the reactor is heated to 50 °C and then 40.4g (60ml) of isoprene is added via an attached ampoule with stirring. After heating for 5 hours at 50-55 °C, a 2ml aliquot of poly(isoprenyl)lithium is removed via a sample port, and the

25

30

sample is quenched with methanol. The sample port is sealed off with a hand torch. Analysis of the base polymer by SEC affords ( $M_n = 43,000$  g/mol, PDI = 1.10). After raising the temperature to 60 °C, 0.74ml of divinylbenzene (55% purity, 0.001mol) is added to provide a

5 [DVB]/[poly(isoprenyl)lithium] = 3. After stirring at 60 °C for 9 hours, the reaction is terminated by addition of 1.5ml of degassed methanol. The resulting polymer is precipitated into methanol two times and dried in a vacuum oven. The polymer is analyzed by SEC and by  $^1\text{H}$  NMR spectroscopy. The polymer molecular weight by SEC analysis (polyisoprene

10 standards) corresponds to  $M_n = 250,000$ , by SEC, linear polyisoprene standard, and 470,000 by universal calibration method and  $M_w/M_n = 1.40$ . The amount of unlinked polyisoprene corresponds to approximately 12 wt.%. The  $^1\text{H}$  NMR spectrum of the final polymer exhibits peaks at  $\delta = 0.88$  and 0.844 ppm corresponding to the (tert-butyldimethylsilyloxy) and sec-

15 butyl end groups, respectively. The resulting polymer is optionally hydrogenated.

#### EXAMPLE 6 (Hypothetical)

##### Deprotection of Functionalized Star Polymer of Example 5

20

A 1.00 gram sample of the polymer prepared in Example 5 is dissolved in 10ml of tetrahydrofuran containing 3 drops of 1.37N aqueous HCl. The mixture is heated at reflux for 4 hours. The reaction mixture is allowed to cool to room temperature, the solvent is removed, and the

25 polymer is vacuum dried. The  $^1\text{H}$  NMR spectrum of the polymer exhibits no peaks corresponding to the (tert-butyldimethylsilyloxy) end group at  $\delta = 0.89\text{ppm}$ .

#### EXAMPLE 7 (Hypothetical)

##### Preparation of Functionalized Star Polymer

30

A star polymer with functionalized and non-functionalized arms is produced by purging an all-glass, high vacuum reactor with dry argon and charging it with 0.273 mmol of hexamethyleneimino-1-propyllithium (0.91ml, 0.3M in cyclohexane, chain-extended with 2 units of isoprene) and 0.273 mmol of sec-butyllithium (0.21ml, 1.3M in cyclohexane) under a positive argon pressure. Purified, dry cyclohexane (200ml) is distilled directly into the reactor followed by removal from the vacuum line by heat sealing with a hand torch. Next, the reactor is heated to 50 °C and then 10.6g (15.6ml) of isoprene is added via an attached ampoule with stirring. After heating for 5 hours at 50-55 °C, a 2ml aliquot of poly(isoprenyl)lithium is removed via a sample port, and the sample is quenched with methanol. The sample port is sealed off with a hand torch. Analysis of the base polymer by SEC affords ( $M_n = 29,000$  g/mol). After raising the temperature to 60 °C, 0.26ml of divinylbenzene (55% purity, 0.001mol) is added to provide a [DVB]/[poly(isoprenyl)lithium] = 3. After stirring at 60 °C for 9 hours, the reaction is terminated by addition of 1.5ml of degassed methanol. The resulting polymer is precipitated into methanol two times and is dried in a vacuum oven. The polymer is analyzed by SEC and by  $^1\text{H}$  NMR spectroscopy. The polymer molecular weight by SEC analysis (polyisoprene standards) corresponds to  $M_n = 235,000$  and  $M_w/M_n = 1.13$ . The amount of unlinked polyisoprene corresponds to approximately 16 wt.%. The  $^1\text{H}$  NMR spectrum of the final polymer exhibits peaks at  $\delta = 2.20$  and 0.844 ppm corresponding to the methylenes adjacent to nitrogen and sec-butyl groups, respectively.

The resultant elastomeric product provided excellent cross-linking properties when used as an additive to tire rubber/ carbon-black vulcanizates.



Preparation of a Block Copolymer from the Deprotected Polyisoprene  
Multiarm Polymer of Example 4.

A weight of 30.00 grams of the deprotected polymer of Example 4 is  
5 dissolved in 300 ml of cyclohexane and treated with 1.05 g of methacryloyl  
chloride and 1.00 g of pyridine at 35-45 °C with stirring for a period of 8 hr.  
The mixture is poured into an equal volume of water and stirred thoroughly.  
The organic layer is separated, washed several times with water, and dried.  
The methacrylate-terminated polymer solution is treated further with 10.00  
10 grams of styrene in the presence of an organic peroxide at 35-50 °C over a  
period of several hours to yield a solution of a segmented block multi-arm  
star possessing outer segments of styrene attached to inner segments of  
hydrogenated polyisoprene on each of the deprotected arms of the polymer.

15 EXAMPLE 12. (Hypothetical)

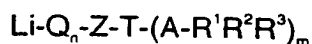
Preparation of a Segmented Block Copolymer from the Deprotected  
Polyisoprene Multiarm Polymer of Example 4.

A 500 ml flask is charged with 200 ml of water, 250 ml of methylene  
20 chloride, one ml of triethylamine, 1.0 gram of p-tert-butylphenol, 5.9 g  
(0.0007 moles) of the hydrogenated, deprotected polymer of Example 4, and  
50.0 grams (0.22 moles) of bisphenol A. With stirring, phosgene is  
introduced into the flask at a rate of 1 gram/min. for 60 minutes while the pH  
is maintained at 10.5 to 11.5 by appropriate addition of 50% aq. NaOH. The  
25 layers are separated, the organic layer is washed with 3 wt% HCl until the  
washings remain acidic, and the organic layer is then washed with water.  
The resin is precipitated from solution into methanol and dried.

What is claimed is:

1. Multi-branched or star-shaped polymers having mixed functional and non-functional ends produced by a process characterized by the steps  
5 of:

(a) polymerizing conjugated alkadienes, selected from butadiene, isoprene and alkenylsubstituted aromatic compounds selected from styrene alpha-methylstyrene, singly, sequentially, or as mixtures thereof, in a liquid reaction medium, at a temperature of -30 °C to 150 °C, for a period of at  
10 least one hour, with mixtures of (a) alkylolithium initiators, selected from n-butyllithium, sec-butyllithium, and tert-butyllithium and (b) protected functional organolithium initiators, having the formula:



15 where Q is an unsaturated hydrocarbyl group derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds, or mixtures of one or more dienes with one or more alkenylaromatic compounds into the Li-Z linkage at a carbon-lithium bond  
20 thereof ; Z is defined as a branched or straight chain hydrocarbyl connecting group containing 3 to 25 carbon atoms; T is an element selected from the group of oxygen, sulfur, and nitrogen; (A-R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>)<sub>m</sub> is a protecting group in which A is an element selected from Group IVa of the Periodic Table of the Elements, as exemplified by carbon and silicon; R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are  
25 independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms; m is 1 when T is oxygen or sulfur and 2  
30 when T is nitrogen; and n is an integer from 0 to 5, to produce protected "living" polymer anions;

(b) Reacting the living polymer anions with a polyfunctional linking compound selected from silicon tetrachloride, tin tetrachloride, phosphorus trichloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes, and mixtures of these compounds at a temperature of 20 °C to 135 °C, for a period of at least one hour, to produce multi-arm star polymers, followed by termination with a protic terminating agent;

(c) Removing the protecting group to produce functionalized multichelic multi-arm or star polymers with hydroxyl, sulfhydryl, or amino groups on the end of some of the arms of the multi-arm or star polymers.

(d) Reaction of the functionalized groups on the ends of the arms of the multi-arm or star polymers with a selected difunctional or polyfunctional comonomer or comonomers selected from the group consisting of organic dicarboxylic acids, organic polycarboxylic acids, organic diisocyanates, organic polyisocyanates, organic diamides, organic polyamides, cyclic amides, organic diols, organic polyols, ethylene oxide in the presence of potassium butoxide, and methacryloyl chloride, acryloyl chloride, or styrenyldimethylchlorosilane, the last three of which are subsequently copolymerized with a free radically polymerizable monomer.

(e) Recovering the multi-arm star polymers from the reaction medium.

2. The multi-arm or star polymer of claim 1 characterized in that the protected functional initiator was selected from the group comprising omega-(tert-alkoxy)-1-alkyllithiums, omega-(tert-alkoxy)-1-alkyllithiums chain extended with conjugated alkadienes or alkenylsubstituted aromatic compounds, omega-(tert-alkylthio)-1-alkyllithiums, omega-(tert-alkylthio)-1-alkyllithiums chain extended with conjugated alkadienes or alkenylsubstituted aromatic compounds, omega-(tert-butoxydimethylsilyloxy)-1-alkyllithiums, omega-(tert-butoxydimethylsilylthio)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums chain-extended with conjugated alkadienes or

alkenylsubstituted aromatic compounds, and omega-(bis-tert-alkylsilylamino)-1-alkyllithiums .

3. The multi-arm or star polymer of claim 1 characterized in that the protected functional initiator was selected from 3-(1,1-dimethylethoxy)-1-propyllithium, 3-(1,1-dimethylethoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethoxy)-1-butyllithium, 5-(1,1-dimethylethoxy)-1-pentyllithium, 6-(1,1-dimethylethoxy)-1-hexyllithium, 8-(1,1-dimethylethoxy)-1-octyllithium, 3-(1,1-dimethylpropoxy)-1-propyllithium, 3-(1,1-dimethylpropoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropoxy)-1-butyllithium, 5-(1,1-dimethylpropoxy)-1-pentyllithium, 6-(1,1-dimethylpropoxy)-1-hexyllithium, 8-(1,1-dimethylpropoxy)-1-octyllithium, 3-(t-butyldimethylsilyloxy)-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 4-(t-butyldimethylsilyloxy)-1-butyllithium, 5-(t-butyldimethylsilyloxy)-1-pentyllithium, 6-(t-butyldimethylsilyloxy)-1-hexyllithium, 8-(t-butyldimethylsilyloxy)-1-octyllithium and 3-(trimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 3-(dimethylamino)-1-propyllithium, 3-(dimethylamino)-2-methyl-1-propyllithium, 3-(dimethylamino)-2,2-dimethyl-1-propyllithium, 4-(dimethylamino)-1-butyllithium, 5-(dimethylamino)-1-pentyllithium, 6-(dimethylamino)-1-hexyllithium, 8-(dimethylamino)-1-propyllithium, 3-(hexamethyleneimino)-1-propyllithium, 4-(hexamethyleneimino)-1-butyllithium, 5-(hexamethyleneimino)-1-pentyllithium, 6-(hexamethyleneimino)-1-hexyllithium, 8-(hexamethyleneimino)-1-octyllithium, 3-(t-butyldimethylsilylthio)-1-propyllithium, 3-(t-butyldimethylsilylthio)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilylthio)-2,2-dimethyl-1-propyllithium, 4-(t-butyldimethylsilylthio)-1-butyllithium, 6-(t-butyldimethylsilylthio)-1-hexyllithium, 3-(trimethylsilylthio)-2,2-dimethyl-1-propyllithium, 3-(1,1-dimethylethylthio)-1-propyllithium, 3-(1,1-dimethylethylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylethylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-

dimethylethylthio)-1-butyllithium, 5-(1,1-dimethylethylthio)-1-pentyllithium, 6-(1,1-dimethylethylthio)-1-hexyllithium, 8-(1,1-dimethylethylthio)-1-octyllithium, 3-(1,1-dimethylpropylthio)-1-propyllithium, 3-(1,1-dimethylpropylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropylthio)-1-butyllithium, 5-(1,1-dimethylpropylthio)-1-pentyllithium, 6-(1,1-dimethylpropylthio)-1-hexyllithium, and 8-(1,1-dimethylpropylthio)-1-octyllithium, and their more hydrocarbon soluble analogs derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds or mixtures of one or more dienes with one or more alkenylaromatic compounds at the lithium carbon bond .

4. The product of Claim 1 further comprising multi-arm or star polymers hydrogenated at a temperature between 25 and 150 °C after forming the multi-arm or star polymer and prior to removing the protecting groups to produce a functionalized multichelical multi-arm or star polymer with protected functional groups on the ends of some of the arms of the polymer.

5. The product of claim 1 further comprising the multi-arm star polymers hydrogenated after deprotection of the polymer at a temperature between 25 and 150 °C to produce a saturated, functionalized multichelical multi-arm or star polymer with functional groups on the ends of some of the arms of the polymer.

6. The product of Claim 4 characterized in that the hydrogenation was continued until at least 90% of of the aliphatic unsaturation has been saturated.

7. The product of Claim 5 characterized in that the hydrogenation was continued until at least 90% of of the aliphatic unsaturation has been saturated.

8. The product of Claim 4 characterized in that the hydrogenation was continued until at least 95% of of the aliphatic unsaturation has been saturated.

9. The process of Claim 5 characterized in that the hydrogenation was continued until at least 95% of of the aliphatic unsaturation has been saturated.

10. The multi-arm or star polymer of Claim 1 characterized in that the  
5 protecting group has been removed from the functional group.

11. The multi-arm or star polymer of Claim 3 characterized in that the protecting group has been removed from the functional group.

12. The multi-arm or star polymer of Claim 1 characterized in that the mole percentage of protected functional organolithium initiator in the total  
10 lithium initiator charge was between 2 and 98.

13. The product of Claim 1 characterized in that the polyfunctional linking compounds were selected from chlorosilanes, chlorostannanes, isomeric divinylbenzenes, isomeric diisopropenylbenzenes, isomeric trivinylbenzenes, isomeric divinyl-naphthalenes, isomeric  
15 trivinyl-naphthalenes, and 1,3,5 - tris(1-phenylethenyl)benzene.

14. The multi-arm or star polymer of Claim 1 characterized in that the conjugated alkadiene polymerized is butadiene, the alkyl-lithium was sec-butyl-lithium, the omega protected functional organolithium initiator was selected from the group consisting of: 3-(1,1-dimethylethoxy)-1-  
20 propyl-lithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenyl-substituted aromatics selected from styrene and alpha-methylstyrene; 3-(1,1-dimethylpropoxy)-1-propyl-lithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenyl-substituted aromatics selected from styrene and alpha-  
25 methylstyrene; 3-(1,1-dimethylethylthio)-1-propyl-lithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene, and alkenyl-substituted aromatics selected from styrene and alpha-methylstyrene; 3-(dimethylamino)-1-propyl-lithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene, and alkenyl-substituted  
30 aromatics selected from styrene and alpha-methylstyrene; 3-(tert-butyl-dimethylsilylthio)-1-propyl-lithium and 3-(tert-butyl-dimethylsilyloxy)-1-

propyllithium and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

15        5        15. The multi-arm or star polymer of Claim 1 characterized in that the conjugated alkadiene polymerized is isoprene, the alkyllithium is sec-butyllithium, the protected functional organolithium initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with isoprene; 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with isoprene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain  
10        extended with isoprene, 3-(dimethylamino)-1-propyllithium, chain extended with isoprene, 3-(tert-butyl dimethylsilylthio)-1-propyllithium and 3-(tert-butyl dimethylsilyloxy)-1-propyllithium and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenyl benzenes, and isomeric  
15        divinylbenzenes.

16. The multi-arm or star polymer of Claim 1 characterized in that the mixture of conjugated alkadiene and alkenylaromatic compound polymerized by the alkyllithium consists of butadiene and styrene, the alkyllithium initiator is sec-butyllithium, the protected functional initiator is  
20        selected from the group consisting of: 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene, and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene; 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene,  
25        and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene; 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene, and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene;  
30        3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene, and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene; 3-(tert-

butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenyl benzenes and isomeric divinylbenzenes.

5           17. The multi-arm or star polymer of Claim 1 characterized in that the conjugated alkadiene and alkenylaromatic compound polymerized sequentially were butadiene and styrene, the alkyllithium initiator is sec-butyllithium, the protected functional initiator is selected from the group consisting of: 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a  
10 conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene; 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene, or alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-  
15 dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene, or alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene, or alkenylsubstituted  
20 aromatics selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium, and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenyl benzenes and isomeric divinylbenzenes.

25           18. The multi-arm or star polymer of Claim 1 characterized in that the mixture of conjugated alkadiene and alkenylaromatic compound polymerized by the alkyllithium were isoprene and styrene, the alkyllithium initiator is sec-butyllithium, the protected functional initiator is selected from the group consisting of: 3-(1,1-dimethylethoxy)-1-propyllithium, chain  
30 extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-



methylystyrene; 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylystyrene; 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with  
5 a conjugated alkadiene selected from butadiene, isoprene, and alkenylsubstituted aromatics selected from styrene and alpha-methylystyrene; 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylystyrene; 3-(tert-  
10 butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

19. The multi-arm or star polymer of Claim 1 characterized in that the  
15 conjugated alkadiene and alkenylaromatic compound polymerized sequentially were isoprene and styrene, the alkyllithium initiator is sec-butyllithium, the protected functional initiator is selected from the group consisting of: 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and  
20 alkenylsubstituted aromatics selected from styrene and alpha-methylystyrene; 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene, and alkenylsubstituted aromatics selected from styrene and alpha-methylystyrene; 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated  
25 alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylystyrene; 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylystyrene; 3-(tert-butyldimethylsilylthio)-1-  
30 propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group consisting of

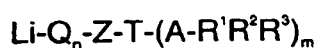
silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

20. The multi-arm or star polymer of Claim 1 characterized in that the conjugated alkadiene polymerized was butadiene, the alkylolithium initiator  
5 was n-butyllithium, the protected functional initiator was selected from the group consisting of; 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene; 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated  
10 alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene; 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene, and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene; 3-  
15 (dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene; 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group consisting of  
20 silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

21. Multi-branched or star-shaped polymers having mixed functional and non-functional ends produced by a process characterized by the steps of:

25 (a) polymerizing conjugated alkadienes, comprising the group of butadiene and isoprene, or alkenylsubstituted aromatic compounds, comprising the group of styrene and alpha-methylstyrene singly, sequentially, or as mixtures thereof, in a liquid reaction medium, at a temperature of -30 °C to 150 °C, for a period of at least one hour, separately  
30 with (a) alkylolithium initiators, comprising the group of n-butyllithium, sec-

butyllithium, and tert-butyllithium and (b) protected functional organolithium initiators, having the formula:



5

where Q is an unsaturated hydrocarbyl group derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds, or mixtures of one or more dienes with one or more alkenylaromatic compounds into the Li-Z linkage at a carbon-lithium bond thereof ; Z is defined as a branched or straight chain hydrocarbyl connecting group containing 3 to 25 carbon atoms; T is an element selected from the group of oxygen, sulfur, and nitrogen; (A-R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>)<sub>m</sub> is a protecting group in which A is an element selected from Group IVa of the Periodic Table of the Elements; R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms; m is 1 when T is oxygen or sulfur and 2 when T is nitrogen; and n is an integer from 0 to 5, to separately produce protected "living" polymer anions;

20

(b) Mixing the separately produced "living" anions, then reacting the living polymer anions with a compound selected from the group of polyfunctional linking compounds, as exemplified by silicon tetrachloride, tin tetrachloride, phosphorus trichloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes, and mixtures of these compounds at a temperature of 20 °C to 135 °C, for a period of at least one hour, to produce multi-arm star polymers;

25

(c) Removing the protecting group to produce functionalized multichelic multi-arm or star polymers with hydroxyl, sulfhydryl or amino groups on the ends of some of the arm of the multi-arm or star polymers.

30

(d) Reaction of the functional groups on the ends of the arms of the polymer with a selected difunctional or polyfunctional comonomer or comonomers selected from the group consisting of organic dicarboxylic acids, organic polycarboxylic acids, organic diisocyanates, organic polyisocyanates, organic diamides, organic polyamides, cyclic amides, organic diols, organic polyols, ethylene oxide in the presence of potassium butoxide, and methacryloyl chloride, acryloyl or styrenyldimethylchlorosilane the last three of which are subsequently copolymerized with a free radically polymerizable monomer.

(e) Recovering the multi-arm star polymers from the reaction medium.

22. The multi-arm or star polymer of claim 21 characterized in that the protected functional initiator was selected from the group comprising omega-(tert-alkoxy)-1-alkyllithiums, omega-(tert-alkoxy)-1-alkyllithiums chain extended with conjugated alkadienes or alkenylsubstituted aromatic compounds, omega-(tert-alkylthio)-1-alkyllithiums, omega-(tert-alkylthio)-1-alkyllithiums chain extended with conjugated alkadienes or alkenylsubstituted aromatic compounds, omega-(tert-butoxydimethylsilyloxy)-1-alkyllithiums, omega-(tert-butoxydimethylsilylthio)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums chain-extended with conjugated alkadienes or alkenylsubstituted aromatic compounds, and omega-(bis-tert-alkylsilylamino)-1-alkyllithiums .

23. The multi-arm or star polymer of claim 21 characterized in that the protected functional initiator was selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, 3-(1,1-dimethylethoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethoxy)-1-butyllithium, 5-(1,1-dimethylethoxy)-1-pentyllithium, 6-(1,1-dimethylethoxy)-1-hexyllithium, 8-(1,1-dimethylethoxy)-1-octyllithium, 3-(1,1-dimethylpropoxy)-1-propyllithium, 3-(1,1-dimethylpropoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-

dimethylpropoxy)-1-butyllithium, 5-(1,1-dimethylpropoxy)-1-pentyllithium, 6-(1,1-dimethylpropoxy)-1-hexyllithium, 8-(1,1-dimethylpropoxy)-1-octyllithium, 3-(t-butyldimethylsilyloxy)-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 4-(t-butyldimethylsilyloxy)-1-butyllithium, 5-(t-butyldimethylsilyloxy)-1-pentyllithium, 6-(t-butyldimethylsilyloxy)-1-hexyllithium, 8-(t-butyldimethylsilyloxy)-1-octyllithium and 3-(trimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 3-(dimethylamino)-1-propyllithium, 3-(dimethylamino)-2-methyl-1-propyllithium, 3-(dimethylamino)-2,2-dimethyl-1-propyllithium, 4-(dimethylamino)-1-butyllithium, 5-(dimethylamino)-1-pentyllithium, 6-(dimethylamino)-1-hexyllithium, 8-(dimethylamino)-1-propyllithium, 3-(hexamethyleneimino)-1-propyllithium, 4-(hexamethyleneimino)-1-butyllithium, 5-(hexamethyleneimino)-1-pentyllithium, 6-(hexamethyleneimino)-1-hexyllithium, 8-(hexamethyleneimino)-1-octyllithium, 3-(t-butyldimethylsilylthio)-1-propyllithium, 3-(t-butyldimethylsilylthio)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilylthio)-2,2-dimethyl-1-propyllithium, 4-(t-butyldimethylsilylthio)-1-butyllithium, 6-(t-butyldimethylsilylthio)-1-hexyllithium, 3-(trimethylsilylthio)-2,2-dimethyl-1-propyllithium, 3-(1,1-dimethylethylthio)-1-propyllithium, 3-(1,1-dimethylethylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylethylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethylthio)-1-butyllithium, 5-(1,1-dimethylethylthio)-1-pentyllithium, 6-(1,1-dimethylethylthio)-1-hexyllithium, 8-(1,1-dimethylethylthio)-1-octyllithium, 3-(1,1-dimethylpropylthio)-1-propyllithium, 3-(1,1-dimethylpropylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropylthio)-1-butyllithium, 5-(1,1-dimethylpropylthio)-1-pentyllithium, 6-(1,1-dimethylpropylthio)-1-hexyllithium, and 8-(1,1-dimethylpropylthio)-1-octyllithium, and their more hydrocarbon soluble analogs derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds or mixtures of one

or more diene hydrocarbons with one or more alkenylaromatic compounds at the lithium carbon bond.

24. The product of Claim 21 further comprising multi-arm or star polymers hydrogenated at a temperature between 25 and 150 °C after  
5 forming the the multi-arm or star polymer and prior to removing the protecting groups to produce a functionalized hydrogenated multichelic multi-arm or star polymer with protected functional groups on the ends of some of the arms of the polymer.

25. The product of claim 21 further comprising multi-arm or star  
10 polymers hydrogenated after deprotection of the polymer at a temperature between 25 and 150 °C to produce a saturated, functionalized multichelic multi-arm or star polymer with functional groups on the ends of some of the arms of the polymer.

26. The product of Claim 24 characterized in that the hydrogenation  
15 was continued until at least 90% of of the aliphatic unsaturation had been saturated.

27. The product of Claim 25 characterized in that the hydrogenation was continued until at least 90% of of the aliphatic unsaturation had been saturated.

20 28. The product of Claim 24 characterized in that the hydrogenation was continued until at least 95% of of the aliphatic unsaturation had been saturated.

29. The process of Claim 25 characterized in that the hydrogenation was continued until at least 95% of of the aliphatic unsaturation had been  
25 saturated.

30. The multi-arm or star polymer of Claim 21 characterized in that the protecting group has been removed from the functional group.

31. The multi-arm or star polymer of Claim 23 characterized in that the protecting group has been removed from the functional group.

32. The multi-arm or star polymer of Claim 21 characterized in that the mole percentage of protected functional organolithium initiator in the total lithium initiator charge was between 2 and 98.

33. The product of Claim 21 characterized in that the polyfunctional  
5 linking compounds were selected from the group comprising chlorosilanes, chlorostannanes, isomeric divinylbenzenes, isomeric diisopropenylbenzenes, isomeric trivinylbenzenes, isomeric divinylnaphthalenes, isomeric trivinylnaphthalenes, and 1,3,5-tris(1-phenylethenyl)benzene.

10 34. The multi-arm or star polymer of Claim 21 characterized in that the conjugated alkadiene polymerized was butadiene, the alkylolithium was sec-butyllithium, the omega protected functional organolithium initiator was selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene,  
15 isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated  
20 alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium and the  
25 polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

35. The multi-arm or star polymer of Claim 21 characterized in that  
30 the conjugated alkadiene polymerized was isoprene, the alkylolithium was sec-butyllithium, the protected functional organolithium initiator was

selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with isoprene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with isoprene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with isoprene, 3-(dimethylamino)-1-propyllithium, chain extended  
5 with isoprene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenyl benzenes, and isomeric divinylbenzenes.

10 36. The multi-arm or star polymer of Claim 21 characterized in that the mixture of conjugated alkadiene and alkenylaromatic compound polymerized by the alkylolithium consisted of butadiene and styrene, the alkylolithium initiator was sec-butyllithium, the protected functional initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium,  
15 chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene,  
20 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected  
25 from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenyl benzenes and isomeric divinylbenzenes.

30 37. The multi-arm or star polymer of Claim 21 characterized in that the conjugated alkadiene and alkenylaromatic compound polymerized



sequentially were butadiene and styrene, the alkyllithium initiator was sec-butyllithium, the protected functional initiator was selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and

5 alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated

10 alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium, and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the

15 polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenyl benzenes and isomeric divinylbenzenes.

38. The multi-arm or star polymer of Claim 21 characterized in that

20 the mixture of conjugated alkadiene and alkenylaromatic compound polymerized by the alkyllithium consisted of isoprene and styrene, the alkyllithium initiator was sec-butyllithium, the protected functional initiator was selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from

25 butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with

30 a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene,

3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(tert-butyltrimethylsilylthio)-1-propyllithium and 3-(tert-butyltrimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound was selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

39. The multi-arm or star polymer of Claim 21 characterized in that the conjugated alkadiene and alkenylaromatic compound polymerized sequentially were isoprene and styrene, the alkylolithium initiator was sec-butyllithium, the protected functional initiator was selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(tert-butyltrimethylsilylthio)-1-propyllithium and 3-(tert-butyltrimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

40. The multi-arm or star polymer of Claim 21 characterized in that the conjugated alkadiene being polymerized was butadiene, the alkylolithium initiator was n-butyllithium, the protected functional initiator was selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain

extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and

5 alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene

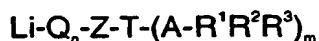
10 selected from butadiene, isoprene and alkenylsubstituted aromatics selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and

15 isomeric divinylbenzenes.

41. The process to produce multi-branched or star-shaped polymers having mixed functional and non-functional ends characterized by the steps of:

(A) polymerizing conjugated alkadienes selected from butadiene, isoprene and alkenylsubstituted aromatic compounds selected from styrene and alpha-methylstyrene singly, sequentially, or as mixtures thereof, in a liquid reaction medium, at a temperature of -30 °C to 150 °C, for a period of at least one hour, with mixtures of (a) alkylolithium initiators, comprising the group of n-butyllithium, sec-butyllithium, and tert-butyllithium and (b)

25 protected functional organolithium initiators, having the formula:



where Q is an unsaturated hydrocarbyl group derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds, or mixtures of one or more dienes with one or more

30

alkenylaromatic compounds into the Li-Z linkage at a carbon-lithium bond thereof ; Z is defined as a branched or straight chain hydrocarbyl connecting group containing 3 to 25 carbon atoms; T is an element selected from the group of oxygen, sulfur, and nitrogen;  $(A-R^1R^2R^3)_m$  is a protecting group in which A is an element selected from Group IVa of the Periodic Table of the Elements;  $R^1, R^2$ , and  $R^3$  are independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms; m is 1 when T is oxygen or sulfur and 2 when T is nitrogen; and n is an integer from 0 to 5, to produce protected "living" polymer anions;

(B) Reacting the living polymer anions with a polyfunctional linking compound at a temperature of 20 °C to 135 °C, for a period of at least one hour, to produce multi-arm or star polymers;

(C) Removing the protecting group to produce functionalized multichelic multi-arm or star polymers with hydroxyl, sulfhydryl, or amino groups on the end of some of the arms of the star polymers.

(D) Reaction of the functionalized groups on the ends of the arms of the multi-arm or star polymer with a selected difunctional or polyfunctional comonomer or comonomers selected from the group consisting of organic dicarboxylic acids, organic polycarboxylic acids, organic diisocyanates, organic polyisocyanates, organic diamides, organic polyamides, cyclic amides, organic diols, organic polyols, ethylene oxide in the presence of potassium butoxide and methacryloyl chloride, acryloyl chloride, or styrenyldimethylchlorosilane, the last three of which are subsequently copolymerized with a free radically polymerizable monomer.

(E) Recovering the multi-arm or star polymers from the reaction medium.

42. The process of claim 41 characterized in that the protected functional initiator is selected from the group comprising omega-(tert-

- alkoxy)-1-alkyllithiums, omega-(tert-alkoxy)-1-alkyllithiums chain extended with conjugated alkadienes or alkenylsubstituted aromatic compounds, omega-(tert-alkylthio)-1-alkyllithiums, omega-(tert-alkylthio)-1-alkyllithiums chain extended with conjugated alkadienes or alkenylsubstituted aromatic compounds, omega-(tert-butoxydimethylsilyloxy)-1-alkyllithiums, omega-(tert-butoxydimethylsilylthio)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums chain-extended with conjugated alkadienes or alkenylsubstituted aromatic compounds, and omega-(bis-tert-alkylsilylamino)-1-alkyllithiums .
43. The process of claim 41 characterized in that the protected functional initiator is selected from 3-(1,1-dimethylethoxy)-1-propyllithium, 3-(1,1-dimethylethoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethoxy)-1-butyllithium, 5-(1,1-dimethylethoxy)-1-pentyllithium, 6-(1,1-dimethylethoxy)-1-hexyllithium, 8-(1,1-dimethylethoxy)-1-octyllithium, 3-(1,1-dimethylpropoxy)-1-propyllithium, 3-(1,1-dimethylpropoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropoxy)-1-butyllithium, 5-(1,1-dimethylpropoxy)-1-pentyllithium, 6-(1,1-dimethylpropoxy)-1-hexyllithium, 8-(1,1-dimethylpropoxy)-1-octyllithium, 3-(t-butyldimethylsilyloxy)-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 4-(t-butyldimethylsilyloxy)-1-butyllithium, 5-(t-butyldimethylsilyloxy)-1-pentyllithium, 6-(t-butyldimethylsilyloxy)-1-hexyllithium, 8-(t-butyldimethylsilyloxy)-1-octyllithium and 3-(trimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 3-(dimethylamino)-1-propyllithium, 3-(dimethylamino)-2-methyl-1-propyllithium, 3-(dimethylamino)-2,2-dimethyl-1-propyllithium, 4-(dimethylamino)-1-butyllithium, 5-(dimethylamino)-1-pentyllithium, 6-(dimethylamino)-1-hexyllithium, 8-(dimethylamino)-1-propyllithium, 3-(hexamethyleneimino)-1-propyllithium, 4-(hexamethyleneimino)-1-butyllithium, 5-(hexamethyleneimino)-1-pentyllithium, 6-(hexamethyleneimino)-1-hexyllithium, 8-(hexamethyleneimino)-1-

octyllithium, 3-(t-butyldimethylsilylthio)-1-propyllithium, 3-(t-butyldimethylsilylthio)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilylthio)-2,2-dimethyl-1-propyllithium, 4-(t-butyldimethylsilylthio)-1-butyllithium, 6-(t-butyldimethylsilylthio)-1-hexyllithium, 3-(trimethylsilylthio)-2,2-dimethyl-1-propyllithium, 3-(1,1-dimethylethylthio)-1-propyllithium, 3-(1,1-dimethylethylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylethylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethylthio)-1-butyllithium, 5-(1,1-dimethylethylthio)-1-pentyllithium, 6-(1,1-dimethylethylthio)-1-hexyllithium, 8-(1,1-dimethylethylthio)-1-octyllithium, 3-(1,1-dimethylpropylthio)-1-propyllithium, 3-(1,1-dimethylpropylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropylthio)-1-butyllithium, 5-(1,1-dimethylpropylthio)-1-pentyllithium, 6-(1,1-dimethylpropylthio)-1-hexyllithium, and 8-(1,1-dimethylpropylthio)-1-octyllithium. and their more hydrocarbon soluble analogs derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds or mixtures of one or more dienes with one or more alkenylaromatic compounds at the lithium carbon bond.

44. The process of Claim 41 further comprising hydrogenating the multi-arm star polymers at a temperature between 25 and 150 °C after forming the the multi-arm star polymer and prior to removing the protecting groups to produce a functionalized multichelic multi-arm or star polymer with protected functional groups on the ends of some of the arms of the polymer.

45. The process of claim 41 further comprising hydrogenating the multi-arm star polymers after deprotection of the polymer at a temperature between 25 and 150 °C to produce a saturated, functionalized multichelic multi-arm or star polymer with functional groups on the ends of some of the arms of the polymer.

46. The process of Claim 44 characterized in that the hydrogenation is continued until at least 90% of of the aliphatic unsaturation has been saturated.

47. The process of Claim 45 characterized in that the hydrogenation is continued until at least 90% of of the aliphatic unsaturation has been saturated.

5 48. The process of Claim 44 characterized in that the hydrogenation is continued until at least 95% of of the aliphatic unsaturation has been saturated.

49. The process of Claim 45 characterized in that the hydrogenation is continued until at least 95% of of the aliphatic unsaturation has been saturated.

10 50. The process of Claim 41 characterized in that the protecting group has been removed from the functional group.

51. The process of Claim 43 characterized in that the protecting group has been removed from the functional group.

15 52. The process of Claim 41 characterized in that the mole percentage of protected functional organolithium initiator in the total lithium initiator charge is between 2 and 98.

20 53. The process of Claim 41 characterized in that the poly functional linking compound is selected from the group consisting of chlorosilanes, chlorostannanes, isomeric divinylbenzenes, isomeric diisopropenylbenzenes, isomeric trivinylbenzenes, isomeric divinyl naphthalenes, isomeric trivinyl naphthalenes and 1,3,5-tris(1-phenylethenyl)benzene.

25 54. The process of Claim 41 characterized in that the conjugated alkadiene polymerized is butadiene, the alkyl lithium is sec-butyllithium, the omega protected functional organolithium initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with  
30 a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-

methystyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methystyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a  
5 conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methystyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium and the polyfunctional linking compound is selected from the group comprising silicon tetrachloride, tin  
10 tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

55. The process of Claim 41 characterized in that the conjugated alkadiene polymerized is isoprene, the alkylolithium is sec-butyllithium, the protected functional organolithium initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with  
15 isoprene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with isoprene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with isoprene, 3-(dimethylamino)-1-propyllithium, chain extended with isoprene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium and the polyfunctional linking  
20 compound is selected from the group comprising silicon tetrachloride, tin tetrachloride, isomeric diisopropenyl benzenes, and isomeric divinylbenzenes.

56. The process of Claim 41 characterized in that the mixture of conjugated alkadiene and alkenylaromatic compound polymerized by the  
25 alkylolithium consists of butadiene and styrene, the alkylolithium initiator is sec-butyllithium, the protected functional initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-  
30 methystyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and



alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group comprising silicon tetrachloride, tin tetrachloride, isomeric diisopropenyl benzenes and isomeric divinylbenzenes.

57. The process of Claim 41 characterized in that the conjugated alkadiene and alkenylaromatic compound polymerized sequentially are butadiene and styrene, the alkylolithium initiator is sec-butyllithium, the protected functional initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium, and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin

tetrachloride, isomeric diisopropenyl benzenes and isomeric divinylbenzenes.

58. The process of Claim 41 characterized in that the mixture of conjugated alkadiene and alkenylaromatic compound polymerized by the alkylolithium consists of isoprene and styrene, the alkylolithium initiator is sec-butylolithium, the protected functional initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propylolithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propylolithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propylolithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propylolithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propylolithium and 3-(tert-butyldimethylsilyloxy)-1-propylolithium, and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

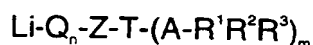
59. The process of Claim 41 characterized in that the conjugated alkadiene and alkenylaromatic compound polymerized sequentially are isoprene and styrene, the alkylolithium initiator is sec-butylolithium, the protected functional initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propylolithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propylolithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene

and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a  
5 conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin  
10 tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

60. The process of Claim 41 characterized in that the conjugated alkadiene being polymerized is butadiene, the alkyllithium initiator is n-butyllithium, the protected functional initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a  
15 conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-  
20 methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and  
25 alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group consisting of silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

61. The process to prepare multi-branched or star-shaped polymers having mixed functional and non-functional ends produced by a process characterized by the steps of:

- (A) polymerizing conjugated alkadienes, selected from the group of butadiene and isoprene, and alkenylsubstituted aromatic compounds selected from styrene and alpha-methylstyrene singly, sequentially, or as mixtures thereof, in a liquid reaction medium, at a temperature of -30 °C to 150 °C, for a period of at least one hour, separately with (a) alkyllithium initiators, selected from n-butyllithium, sec-butyllithium, and tert-butyllithium and (b) protected functional organolithium initiators, having the formula:



- where Q is an unsaturated hydrocarbyl group derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds, or mixtures of one or more dienes with one or more alkenylaromatic compounds into the Li-Z linkage at a carbon-lithium bond thereof; Z is defined as a branched or straight chain hydrocarbyl connecting group containing 3 to 25 carbon atoms; T is an element selected from the group of oxygen, sulfur, and nitrogen;  $(\text{A-R}^1\text{R}^2\text{R}^3)_m$  is a protecting group in which A is an element selected from Group IVa of the Periodic Table of the Elements, as exemplified by carbon and silicon;  $\text{R}^1, \text{R}^2$ , and  $\text{R}^3$  are independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms; m is 1 when T is oxygen or sulfur and 2 when T is nitrogen; and n is an integer from 0 to 5, to separately produce protected "living" polymer anions;

- (B) Mixing the separately produced "living" anions, then reacting the living polymer anions with a polyfunctional linking compound at a

temperaure of 20 °C to 135 °C, for a period of at least one hour, to produce multi-arm or star polymers;

(C) Removing the protecting group to produce functionalized multichelic multi-arm or star polymers with hydroxyl, sulfhydryl, or amino groups on the ends of some of the arm of the multi-arm or star polymers;

(D) Reaction of the functional groups on the ends of the arms of the polymer with a selected difunctional or polyfunctional comonomer or comonomers selected from the group consisting of organic dicarboxylic acids, organic polycarboxylic acids, organic diisocyanates, organic polyisocyanates, organic diamides, organic polyamides, cyclic amides, organic diols, organic polyols, ethylene oxide in the presence of potassium butoxide, and methacryloyl chloride, acryloyl chloride, or styrenyldimethylchlorosilane, the last three of which are subsequently copolymerized with a free radically polymerizable monomer.

(E) Recovering the multi-arm star polymers from the reaction medium.

62. The process of claim 61 characterized in that the protected functional initiator is selected from the group comprising omega-(tert-alkoxy)-1-alkyllithiums, omega-(tert-alkoxy)-1-alkyllithiums chain extended with conjugated alkadienes or alkenylsubstituted aromatic compounds, omega-(tert-alkylthio)-1-alkyllithiums, omega-(tert-alkylthio)-1-alkyllithiums chain extended with conjugated alkadienes or alkenylsubstituted aromatic compounds, omega-(tert-butoxydimethylsilyloxy)-1-alkyllithiums, omega-(tert-butoxydimethylsilylthio)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums chain-extended with conjugated alkadienes or alkenylsubstituted aromatic compounds, and omega-(bis-tert-alkylsilylamino)-1-alkyllithiums .

63. The process of claim 61 characterized in that the protected functional initiator is selected from the group of 3-(1,1-dimethylethoxy)-1-propyllithium, 3-(1,1-dimethylethoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethoxy)-1-

butyllithium, 5-(1,1-dimethylethoxy)-1-pentyllithium, 6-(1,1-dimethylethoxy)-  
1-hexyllithium, 8-(1,1-dimethylethoxy)-1-octyllithium, 3-(1,1-  
dimethylpropoxy)-1-propyllithium, 3-(1,1-dimethylpropoxy)-2-methyl-1-  
propyllithium, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-  
5 dimethylpropoxy)-1-butyllithium, 5-(1,1-dimethylpropoxy)-1-pentyllithium, 6-  
(1,1-dimethylpropoxy)-1-hexyllithium, 8-(1,1-dimethylpropoxy)-1-octyllithium,  
3-(t-butyl dimethylsilyloxy)-1-propyllithium, 3-(t-butyl dimethylsilyloxy)-2-  
methyl-1-propyllithium, 3-(t-butyl dimethylsilyloxy)-2,2-dimethyl-1-  
propyllithium, 4-(t-butyl dimethylsilyloxy)-1-butyllithium, 5-(t-  
10 butyl dimethylsilyloxy)-1-pentyllithium, 6-(t-butyl dimethylsilyloxy)-1-  
hexyllithium, 8-(t-butyl dimethylsilyloxy)-1-octyllithium and 3-  
(trimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 3-(dimethylamino)-1-  
propyllithium, 3-(dimethylamino)-2-methyl-1-propyllithium, 3-  
(dimethylamino)-2,2-dimethyl-1-propyllithium, 4-(dimethylamino)-1-  
15 butyllithium, 5-(dimethylamino)-1-pentyllithium, 6-(dimethylamino)-1-  
hexyllithium, 8-(dimethylamino)-1-propyllithium, 3-(hexamethyleneimino)-1-  
propyllithium, 4-(hexamethyleneimino)-1-butyllithium, 5-  
(hexamethyleneimino)-1-pentyllithium, 6-(hexamethyleneimino)-1-  
hexyllithium, 8-(hexamethyleneimino)-1-octyllithium, 3-(t-  
20 butyl dimethylsilylthio)-1-propyllithium, 3-(t-butyl dimethylsilylthio)-2-methyl-1-  
propyllithium, 3-(t-butyl dimethylsilylthio)-2,2-dimethyl-1-propyllithium, 4-(t-  
butyl dimethylsilylthio)-1-butyllithium, 6-(t-butyl dimethylsilylthio)-1-  
hexyllithium, 3-(trimethylsilylthio)-2,2-dimethyl-1-propyllithium, 3-(1,1-  
dimethylethylthio)-1-propyllithium, 3-(1,1-dimethylethylthio)-2-methyl-1-  
25 propyllithium, 3-(1,1-dimethylethylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-  
dimethylethylthio)-1-butyllithium, 5-(1,1-dimethylethylthio)-1-pentyllithium, 6-  
(1,1-dimethylethylthio)-1-hexyllithium, 8-(1,1-dimethylethylthio)-1-  
octyllithium, 3-(1,1-dimethylpropylthio)-1-propyllithium, 3-(1,1-  
dimethylpropylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropylthio)-2,2-  
30 dimethyl-1-propyllithium, 4-(1,1-dimethylpropylthio)-1-butyllithium, 5-(1,1-

dimethylpropylthio)-1-pentyllithium, 6-(1,1-dimethylpropylthio)-1-hexyllithium, and 8-(1,1-dimethylpropylthio)-1-octyllithium, and their more hydrocarbon soluble analogs derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds or mixtures of one or more dienes with one or more alkenylaromatic compounds at the lithium carbon bond .

64. The process of Claim 61 further comprising hydrogenating the multi-arm star polymers at a temperature between 25 and 150 °C after forming the -multi-arm star polymer and prior to removing the protecting groups to produce a functionalized multichelic multi-arm or star polymer with protected functional groups on the ends of some of the arms of the polymer.

65. The process of claim 61 further comprising hydrogenating the multi-arm star polymers after deprotection of the polymer at a temperature between 25 and 150 °C to produce a saturated, functionalized multichelic multi-arm or star polymer with functional groups on the ends of some of the arms of the polymer.

66. The process of Claim 64 characterized in that the hydrogenation is continued until at least 90% of of the aliphatic unsaturation has been saturated.

67. The process of Claim 65 characterized in that the hydrogenation is continued until at least 90% of of the aliphatic unsaturation has been saturated.

68. The process of Claim 64 characterized in that the hydrogenation is continued until at least 95% of of the aliphatic unsaturation has been saturated.

69. The process of Claim 65 characterized in that the hydrogenation is continued until at least 95% of of the aliphatic unsaturation has been saturated.

70. The process of Claim 61 characterized in that the protecting group has been removed from the functional group.

71. The process of Claim 63 characterized in that the protecting group has been removed from the functional group.

72. The process of Claim 61 characterized in that the mole percentage of omega protected functional organolithium initiator in the total  
5 lithium initiator charge is between 2 and 98.

73. The process of Claim 61 characterized in that the polyfunctional linking compounds are selected from the group consisting of chlorosilanes, chlorostannanes, isomeric divinylbenzenes, isomeric diisopropenylbenzenes, isomeric trivinylbenzenes, isomeric  
10 divinylnaphthalenes, isomeric trivinylnaphthalenes and 1,3,5-tris(1-phenylethenyl)benzene.

74. The process of Claim 61 characterized in that the conjugated alkadiene polymerized is butadiene, the alkylolithium is sec-butyllithium, the omega protected functional organolithium initiator is selected from the group  
15 consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and  
20 alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a  
25 conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium and the polyfunctional linking compound is selected from the group comprising of silicon tetrachloride, tin  
30 tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.



75. The process of Claim 61 characterized in that the conjugated alkadiene polymerized is isoprene, the alkyllithium is sec-butyllithium, the protected functional organolithium initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with  
5 isoprene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with isoprene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with isoprene, 3-(dimethylamino)-1-propyllithium, chain extended with isoprene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium and the polyfunctional linking  
10 compound is selected from the group comprising silicon tetrachloride, tin tetrachloride, isomeric diisopropenyl benzenes, and isomeric divinylbenzenes.

76. The process of Claim 61 characterized in that the mixture of conjugated alkadiene and alkenylaromatic compound polymerized by the  
15 alkyllithium consists of butadiene and styrene, the alkyllithium initiator is sec-butyllithium, the protected functional initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-  
20 methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and  
25 alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-  
30 butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group comprising silicon tetrachloride, tin

tetrachloride, isomeric diisopropenyl benzenes and isomeric divinylbenzenes.

77. The process of Claim 61 characterized in that the conjugated alkadiene and alkenylaromatic compound polymerized sequentially are  
5 butadiene and styrene, the alkylolithium initiator is sec-butyllithium, the protected functional initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-  
10 propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-  
15 methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium, and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking  
20 compound is selected from the group comprising silicon tetrachloride, tin tetrachloride, isomeric diisopropenyl benzenes and isomeric divinylbenzenes.

78. The process of Claim 61 characterized in that the mixture of conjugated alkadiene and alkenylaromatic compound polymerized by the  
25 alkylolithium consists of isoprene and styrene, the alkylolithium initiator is sec-butyllithium, the protected functional initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-  
30 methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and

alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group comprising silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

79. The process of Claim 61 characterized in that the conjugated alkadiene and alkenylaromatic compound polymerized sequentially are isoprene and styrene, the alkylolithium initiator is sec-butyllithium, the protected functional initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group comprising silicon tetrachloride, tin

tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes.

80. The process of Claim 61 characterized in that the conjugated alkadiene being polymerized is butadiene, the alkyllithium initiator is n-butyllithium, the protected functional initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylpropoxy)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(1,1-dimethylethylthio)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(dimethylamino)-1-propyllithium, chain extended with a conjugated alkadiene selected from butadiene, isoprene and alkenylsubstituted aromatics, selected from styrene and alpha-methylstyrene, 3-(tert-butyldimethylsilylthio)-1-propyllithium and 3-(tert-butyldimethylsilyloxy)-1-propyllithium, and the polyfunctional linking compound is selected from the group comprising silicon tetrachloride, tin tetrachloride, isomeric diisopropenylbenzenes and isomeric divinylbenzenes..

81. The product of Claim 1, characterized in that the protecting groups at the terminus of each functional multi-arm or star polymer arm are removed by acidic deprotection.

82. The product of Claim 81, where the hydroxyl functional groups are further reacted with diisocyanates and diols to produce polyurethane blocks as the outer segments of the functional multi-arm or star polymer arms.

83. The product of Claim 82, characterized in that part of the diol is substituted with an acid functional diol and such acid groups further neutralized with tertiary amines to provide dispersibility in water.

84. The product of Claim 83 characterized in that the acid functional diol is dimethylolpropionic acid.

85. The product of Claim 81, characterized in that the hydroxyl functional groups are further reacted with compounds selected from diacids, anhydrides, diamines and lactams to produce polyamide blocks as the outer  
5 segments of the functional multi-arm or star polymer arms.

86. The product of Claim 85 characterized in that part of the diacid or anhydride is substituted by an unsaturated acid or anhydride which produces unsaturated polyester blocks capable of crosslinking with  
10 unsaturated monomers such as styrene by addition of free radical initiators.

87. The product of Claim 86, characterized in that the unsaturated acid or anhydride is selected from fumaric acid or maleic anhydride.

88. The product of Claim 87, characterized in that the hydroxyl groups are further reacted with an anhydride to form a half-ester with free carboxyl  
15 functionality at the terminus of each functional polymer arm.

89. The product of Claim 88, characterized in that the carboxyl functional terminal groups are further reacted with epoxy resins and amine curing agents to form toughened epoxy resin composites.

90. The product of Claim 81, characterized in that the hydroxyl  
20 functional groups are reacted with methacryloyl chloride to form stars with polymerizable alkenyl groups at the terminus of each functional polymer arm.

91. The product of Claim 90, characterized in that acrylic monomers are polymerized, by use of free radical initiators, onto the alkenyl terminal  
25 groups at the terminus of each functional polymer star arm.

92. The product of Claim 91, characterized in that acid functional or amide functional acrylic monomers, are used and which result in polar hydrophilic polymer segments at the end of each functional star polymer arm.

30 93. The product of Claim 90, characterized in that sulfonated styrene and/or 4-vinyl pyridine are polymerized by free radical initiators onto the

terminal alkenyl groups at the terminus of each functional polymer star arm, producing functional polymer segments capable of improving dispersability of the star polymers in lubricating oils.

94. The product of Claim 81, characterized in that the hydroxyl  
5 functional groups are reacted with sulfonyl chloride, along with a tertiary amine catalyst, to form sulfonate functional groups at the terminus of each functional polymer star arm.

95. The product of Claim 94, characterized in that the sulfonate  
10 terminated arms of the stars are reacted with primary amines or ammonia, under heat and pressure, to form star polymers with amine functionality at the terminus of each functional polymer star arm.

96. The product of Claim 88, characterized in that the carboxyl  
15 functional star polymer is reacted with an epoxy resin and an excess of amine to completely react all of the epoxy groups, the excess amine is removed by distillation, and the resulting epoxy-amine adduct is reacted with a water soluble organic or inorganic acid to form water soluble quarternary ammonium containing polymers.

97. The product of Claim 4 or 5, characterized in that the protecting  
20 groups at the terminus of each functional arm are removed by acidic deprotection.

98. The products of Claim 97, characterized in that the hydroxyl  
functional groups are further reacted with diisocyanates and diols to produce polyurethane blocks as the outer segments of the functional star polymer arms.

25 99. The products of Claim 98, characterized in that part of the diol is substituted with an acid functional diol and such acid groups further neutralized with tertiary amines to provide dispersibility in water.

100. The products of Claim 99, characterized in that the acid functional  
diol is dimethylolpropionic acid.

30 101. The products of Claim 97, characterized in that the hydroxyl functional groups are further reacted with compounds selected from the

group of diacids, anhydrides, diamines and lactams to produce polyamide blocks as the outer segments of the functional star polymer arms.

102. The products of Claim 101, characterized in that part of the diacid or anhydride is substituted by an unsaturated acid or anhydride which  
5 produces unsaturated polyester blocks capable of crosslinking with unsaturated monomers such as styrene by addition of free radical initiators.

103. The products of Claim 102, characterized in that the unsaturated acid or anhydride is selected from fumaric acid and maleic anhydride.

104. The products of Claim 97, characterized in that the hydroxyl  
10 groups are further reacted with an anhydride to form a half-ester with free carboxyl functionality at the terminus of each functional star polymer arm.

105. The products of Claim 104, characterized in that the carboxyl functional terminal groups are further reacted with epoxy resins and amine curing agents to form toughened epoxy resin composites.

15 106. The products of Claim 97, characterized in that the hydroxyl functional groups are reacted with methacryloyl chloride to form stars with polymerizable alkenyl groups at the terminus of each functional polymer star arm.

107. The products of Claim 106, characterized in that acrylic monomers  
20 are polymerized, by use of free radical initiators, onto the alkenyl terminal groups at the terminus of each functional polymer star arm.

108. The products of Claim 107, characterized in that acid functional or amide functional acrylic monomers, such as acrylic acid or methacrylic acid, are used and which result in polar hydrophilic polymer segments at the end  
25 of each functional star polymer arm.

109. The products of Claim 108, characterized in that sulfonated styrene and/or 4-vinyl pyridine are polymerized by free radical initiators onto the terminal alkenyl groups at the terminus of each polymer star arm, producing functional polymer segments capable of improving dispersability of the star  
30 polymers in lubricating oils.

110. The products of Claim 97, characterized in that the hydroxyl functional groups are reacted with sulfonyl chloride, along with a tertiary amine catalyst, to form sulfonate functional groups at the terminus of each functional polymer star arm.

5 111. The products of Claim 110, characterized in that the sulfonate terminated arms of the stars are reacted with primary amines or ammonia, under heat and pressure, to form star polymers with amine functionality at the terminus of each functional polymer star arm.

10 112. The products of Claim 104, characterized in that the carboxyl functional star polymer is reacted with an epoxy resin and an excess of amine to completely react all of the epoxy groups, the excess amine is removed by distillation, and the resulting epoxy-amine adduct is reacted with a water soluble organic or inorganic acid to form water soluble quarternary ammonium containing polymers.

15 113. A process for modifying the surface adhesion properties of polyolefins, comprising melt mixing the functional polymer of Claims 1, 4, 5, 81, 82, 85, 86, 88, 90, 91, 92, 94, 95, 97, 98, 101, 102, 104, 106, 107, 108, 110, or 111 with a polyolefin at a level of 1 to 25% by weight based on the polyolefin.

20 114. The process of Claim 113, where the polyolefin is selected from the group comprising low density polyethylene, linear low density polyethylene, high density polyethylene, homopolymers and copolymers of propylene, and polyisobutylene.

115. The product of claim 1 where in the protic terminating agent was selected from water or alcohol.

25 116. The process of claim 21 and 41 characterized in that the element of group IVa is selected from carbon and silicon.

117. The product of claim 92 characterized in that the amide functional acrylic monomer is selected from acrylic and methacrylic acids.



# INTERNATIONAL SEARCH REPORT

Inter:   nal Application No  
PCT/US 96/12380

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6   C08F36/04   C08F12/06   C08F4/46   C08F4/72   C08C19/44  
C08G81/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C08F   C08C   C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 241 239 (SECR DEFENCE) 28 August 1991 see page 7, line 7 - line 34; claims 24,26 ---	1
A	GB,A,2 144 430 (SHELL INT RESEARCH) 6 March 1985 see claim 1 ---	1
P,A	WO,A,95 22566 (FMC CORP) 24 August 1995 see claims 7-20 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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- \*P\* document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

7 November 1996

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/12380

Pat/85 30/12580

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